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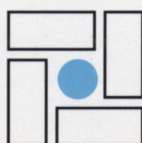
LITHOLOGY AND MINERAL RESOURCES

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Editor-in-Chief
Vladimir N. Kholodov

Academician of the Academy of Natural Sciences
Professor, Doctor of Geology and Mineralogy

**A Journal on Problems of the Theory of
Sedimentary Rock Formation and Ore Genesis**



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Lithology and Mineral Resources

(*Litologiya i Poleznye Iskopaemye*)

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Lithology and Mineral Resources (*Litologiya i Poleznye Iskopaemye*) reviews a wide range of problems related to the formation of sedimentary rocks and ores. Special attention is devoted to comparison of ancient sedimentary rock- and ore formation with present-day processes, as the idea of actualism has always constituted one of the bases of the scientific philosophy of lithologists. A major part of the journal is devoted to comparative analysis of sedimentary processes on continents and in oceans, as well as the genetic aspects of the formation of sedimentary and hydrothermal-sedimentary mineral resources. The journal was founded in 1963 by Academician N. M. Strakhov. It will be of interest to lithologists, petrographers, geochemists, mineralogists, ore geologists and metallogenists, as well as to other geologists, ecologists, researchers of experimental and analytical laboratories, and graduate students.

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The Danube Submarine Fan: Specific Features of the Structure and Sediment Accumulation

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Abstract—Investigations carried out in the upper and middle parts of the Danube Fan revealed a considerable diversity of the accumulated sediments. For example, in the axial part of the main fan valley, during the Pleistocene, predominantly terrigenous, laminated sands and silts accumulated, whereas on the fringing levees, gravity flow deposits, consisting largely of clasts of old claystones and mudstones, were observed. Slumped sediments predominate in the near-wall parts of the valley. Turbidites, which are made up of terrigenous clastic material, are widespread in the middle fan of the river, where they deposited during the Pleistocene both in the distributary channels and on the levees.

In recent years, thanks to the development of new effective methods of investigations of seafloor relief and deep structure (multichannel reflection seismics, multibeam echosounders, and seafloor mapping with sidescan sonars), researchers of different countries came to focus considerable attention on investigations of submarine fans in different areas of the World Ocean.

Submarine fans are thick accumulative geological bodies, containing a large volume of sedimentary material, which was mobilized from drainage areas in central and marginal parts of continents and supplied to the sea along with river discharge during many hundreds of thousands or even millions of years within a relatively narrow strip of a coastal zone. The length of the largest submarine fans, also known as “deep-sea fans” or “fans,” often exceeds many hundred kilometers. Examples are found in large fans, such as the Bengal Fan and the Amazon Fan formed during the largest part of the Neogene and the Pleistocene; consequently, they include different age sedimentary complexes, which replace each other in vertical and lateral directions. The thickness of deposits in the central part of such an accumulative body of a large fan can be in excess of some thousands of meters (*Submarine* ..., 1985).

In addition to the huge deep-sea fans sometimes affecting the evolution of entire sedimentary basins, such as the Gulf of Bengal Basin, there are submarine fans governing the formation of sedimentary cover within only a limited area of a continental margin and in the adjacent part of marine or oceanic basin. The length of these fans does not exceed 200–300 km, and the thickness of the accumulated sediments varies from some hundred meters to a kilometer. Nevertheless, such bodies incorporate many thousands of cubic kilometers of largely terrigenous sediments consisting of both fine-grained and coarse-grained varieties. Examples are

provided by submarine fans formed on continental slopes on the extension of rivers, such as the Nile, the Rhone, the Danube, and others. Interest in the study of these features is provoked by the fact that oil fields were discovered during drilling of the Pleistocene sand beds in the upper Mississippi Fan.

Regardless of the size of submarine fans, there are some common features of their structure. For instance, upper, middle, and lower fans, as well as a fringe fan are normally distinguished in the structure of a submarine fan (Shanmugam and Moliola, 1991). The upper fan implies a central accumulative body, rising from a few meters to a few hundred meters above the surrounding seafloor. Because of this, at earlier stages of marine geological investigations, such topographic features were interpreted as ridges. In doing so, it was considered that they have a tectonic or volcanic nature. However, shortly after, these “ridges” were found to start near mouths of large submarine canyons that continue over the crestal part of the fan as narrow and deep depression (submarine valley). The valley represents a pathway for gravity flows, including turbidity flows, which move from the continental slope. Turbidity flows transport a large volume of sedimentary material dragged over the seafloor or suspended in seawater.

The middle fan is distinguished in the area where the main fan valley breaks down into smaller submarine channels, which, in turn, split apart into even smaller channels poorly expressed in the seafloor relief. The area, which is drained by these narrow and shallow (2 to 5 m) channels, belongs to a lower fan, and the adjacent seafloor is referred to as a fringe fan. Here, turbidity currents virtually terminate all activity, and the material which was brought by them, settles down as a peculiar apron. The system of submarine channels and ravines, the presence of which normally allows cones to be denoted as fans, is not expressed here in the seafloor

relief. Accumulative bodies composed of young sediments and separated from the main fan are often referred to as neofans. They form along the margins of the main fan and largely consist of sands and silts (Nelson *et al.*, 1992; Twichell *et al.*, 1992).

THE SEAFLOOR RELIEF AND STRUCTURE OF THE DANUBE SUBMARINE FAN

The study of the Danube submarine Fan was carried out for several years during the marine training course for students of Geological Faculty by the staff of the Department of Geology and Geochemistry of Fossil Fuels and Department of Seismometry. The study was initially focused on the best topographically expressed part of the accumulative body, onlapping the continental slope by one of its ends and stretching southeastward for more than 100 km. The fan width varies from 30 to 50 km and it rises 250–400 m above the surrounding seafloor (Konyukhov *et al.*, 1988).

The areas of the deep-sea fan which are more distant from the continental slope have thereafter come under the scrutiny of the study. Echosounder and seismoacoustic surveys were conducted along a system of more or less closely spaced lines, as a rule, oriented transversely to the trends of the main topographic features within beforehand specified areas. After the analysis of the seismoacoustic data obtained, the sampling sites were chosen, from which sediment cores were taken with a large-diameter gravity corer. The total length of the seismoacoustic lines, covering only the upper Danube Fan, is more than 600 km (Fig. 1), and a total of 16 cores were recovered from this area.

(1) The upper fan. In the seismoacoustic profiles, which are parallel to the continental slope and are spaced 4 to 8 km apart, one can observe that on the summit of the accumulative body there is a trench up to 200 m deep. It is from 300 to 500 m wide at the bottom but up to 2–3 km wide at the upper edges of its flanks. This trough in reality represents the V-shaped central fan valley and, in essence, is an extension of one of the submarine canyons cutting through the continental slope opposite the Danube River mouth.

Almost the entire stretch of the fan valley is fringed by different-height levees with pointed or conical crests (Fig. 2). These levees build up the upper surface of a seafloor rise divided by the fan valley into two areally unequal (in width) parts. The higher levee, having a peaklike form in some seismoacoustic profiles, extends along the southwestern bank of the fan valley. The elevation of its crest above the bottom of the axial part of the valley can reach 450 m. The opposite, northeastern flank rises not more than 200 m above the valley, and its levee is hardly visible in some profiles.

In the seismic profiles, studied 15 to 20 km away from the continental slope, a different pattern is observed: both levees have approximately the same topographic expression. They do not loom immediately

above the valley, as in the previous case, but are situated some distance from the valley. The fan valley is considerably wider here, and the distance between the opposite levees increases by 2–3 km. In general, the accumulative rise appears to be symmetrical in this area (Fig. 3).

However, the symmetry of the rise is disturbed again toward the south: the southwestern levee is crowned by a flat top, while the levee is absent on the opposite flank of the valley. This seems to have been caused by the northward shift of the fan valley itself and by its incision into the slope of the accumulative body and subsequent erosion of its sediments. This also resulted in the destruction of the northern levee.

The northward valley shift is indicated by its "trace"—darker sectors in the center of the seismoacoustic profile (Fig. 4). The darker sectors are correlated with acoustically opaque sedimentary members accumulated predominantly in the axial part of the central fan valley (Flood, 1987). These submarine channel deposits represented by thin alternation of sands and silts quickly pinch out laterally, being replaced by sediments of other facies. In most of the seismoacoustic profiles, the "channelized" facies can be traced down to a great depth in sediments. In the place where the fan valley migrated over time south—or northward, its trace in sediments shifts in the corresponding direction.

It should be noted that with distance from the continental slope, not only the summit, but also the whole accumulative body becomes asymmetrical. As this takes place, the northeastern slope of the Danube Fan turns out to be steeper than the southwestern one.

The correlation of the seismoacoustic profiles allows the cause of this asymmetry to be established. The point is that south of the recent accumulative rise, another accumulative mound of smaller size, is found. Unlike the recent one, it is buried under a cover of Late Pleistocene–Holocene sediments (Konyukhov and Ivanov, 1989). The crest of this older rise has long been an obstacle for the uniform spreading of sedimentary material. The material mostly accumulated between the summits of both the relic and newly formed bodies that produced a sort of a sedimentary trap for seafloor flows. The outlines of the buried fan are clearly observed in a number of seismoacoustic profiles.

For example, Fig. 5 displays a buried clinoform with a depression that complicate the summital part and represents the relic of an old fan valley. Previously, this valley was surrounded by levees with different heights; the crest of the higher southern levee is still reflected in the seafloor relief, although it was covered by younger sediments. The northeastern slope of the buried fan was probably gentler and had a steplike form. The space between the southern slope of the recent accumulative rise and the top of the buried fan appears now as a flattened submarine plateau, rising almost 200 m above the seafloor in this part of the Black Sea Basin.

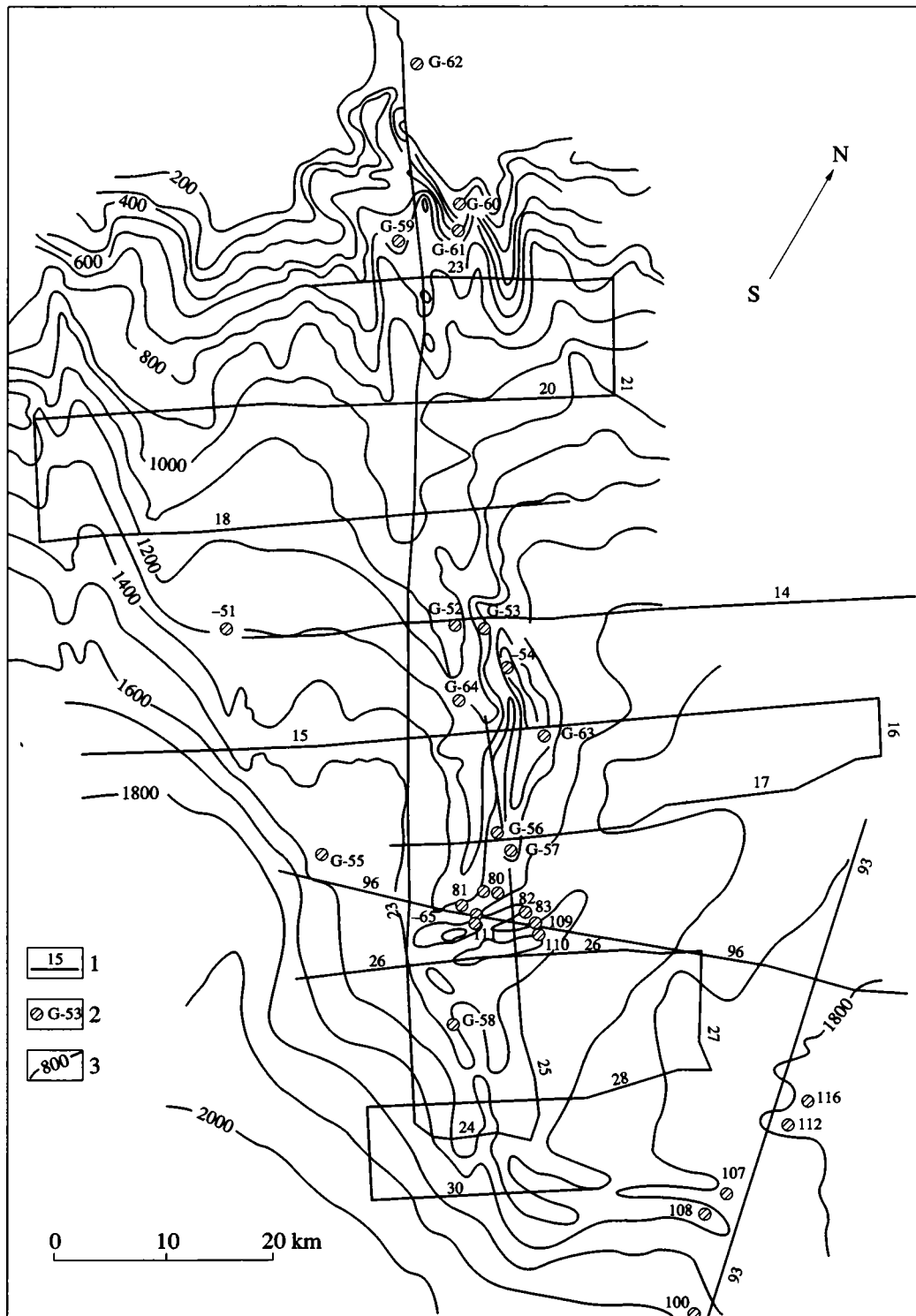


Fig. 1. Location map of seismoacoustic profiles and sampling sites. (1) Seismoacoustic profile and its number, (2) sampling site number, and (3) isobath, m.

The outlines of the old fan are also observed in the seismoacoustic profile running close by the continental slope (Fig. 2). However, here it appears to be separated from the recent fan, because both accumulative features

are divided by a depression. It seems that this fan was formed during the period of activation of another submarine canyon that was fed with sediments derived from the southerly arm of the Danube Delta.

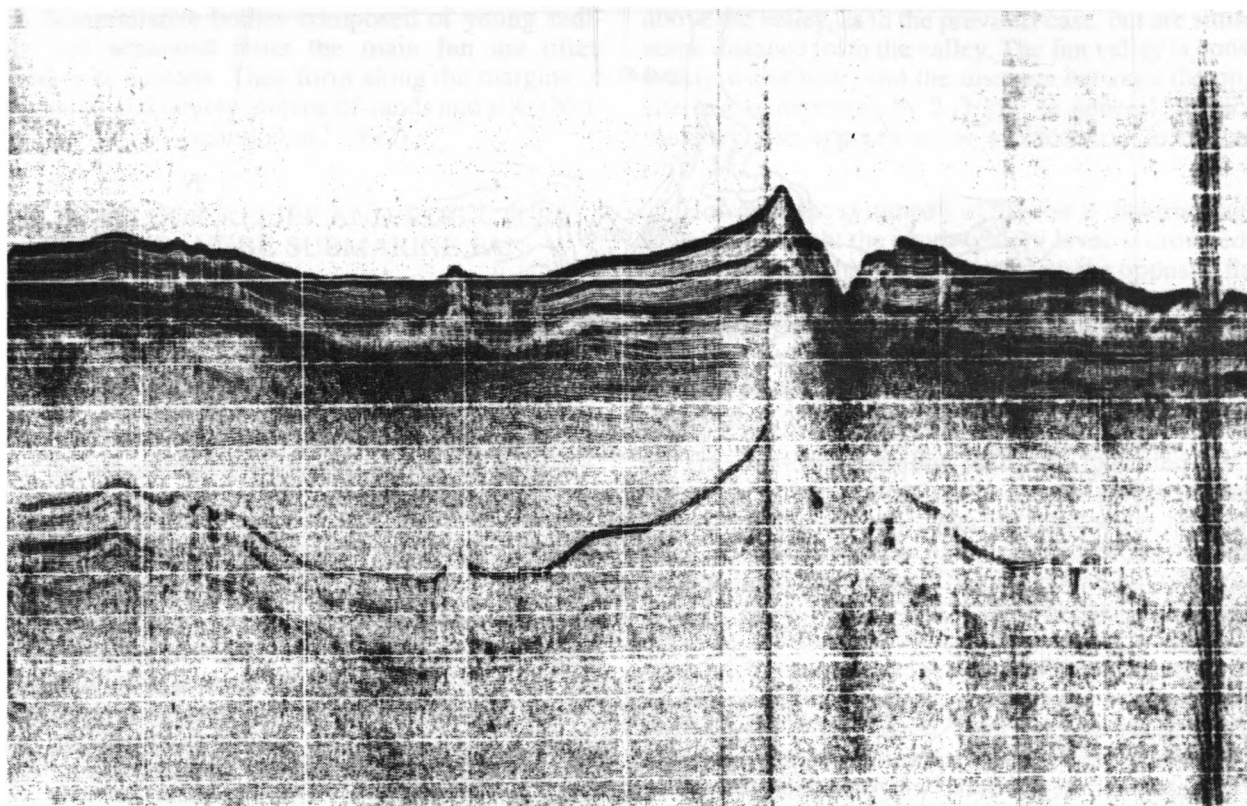


Fig. 2. Seismo-acoustic profile 20 across the fan near the continental slope.

The buried fan is most markedly manifested in profiles 63 (Fig. 5) and 96 (Fig. 6) situated respectively 25 and 30 km from the continental slope. In the first profile, the fan looks asymmetrical: the central fan valley is framed by a levee only along its southern bank, whereas the opposing slope of the rise is rather low and appears to be partially eroded. In profile 96, the same slope is topped with a levee with a pointed crest that previously rose both above the valley and the top of the opposite levee. Indeed, the valley loses here its V-like cross-section and changes into a wide trough filled with stratified sediments.

It is pertinent to note that the relic and recent submarine fans are seen to be merging with increasing distance from the continental slope. For instance, in profile 20 (Fig. 2), the buried rise is offset by 35–40 km from the recent one, and in Profile 96, it is situated virtually under its southwestern slope. Thus, both of them prograded approximately in the same direction (from northwest to southeast), although the older fan developed at an angle rather than perpendicular to the continental slope.

The fan valley passes into a troughlike depression, 4 to 5 km wide, in the distal part of the central rise. The valley trace, which is well-pronounced at the lower levels of the sedimentary sequence beneath the trough, disappears near the top of the sequence (Fig. 6), testify-

ing to the dying out of the fan valley in the distal part of the deep-sea fan. Indeed, here it is covered by young sediments, i.e., it ceased to act as the pathway for sedimentary material transport to the peripheral areas of the deep-sea fan. Hence, the southernmost, distal part of the fan can be considered as a relic feature that began to break down at the end of the Pleistocene.

However, this cannot be said about the entire Danube Fan. Indeed, in the same Profile 96, north of the troughlike depression, a submarine valley surrounded by low levees is found. Its depth from the shoulders to the thalweg is not more than 150 m. A slitlike form of the valley suggests that active gravity flows have recently moved along it, washing out its bottom from suspended sediments and unconsolidated deposits, which slumped from the valley walls. The seismic signature, which implies the presence of channel facies, can be traced here to a moderate depth. The level of the sedimentary sequence, where the seismic trace terminates, coincides with the level beneath the adjacent trough, where a similar trace becomes visible (Fig. 6). It is evident that the latter trough formed after the gravity flows, which moved from the continental slope toward the halistage, cut a new channel that became the main sedimentary pathway in the Late Pleistocene.

This phenomenon seems to be similar to the formation of a meander by a river flowing over a plain.

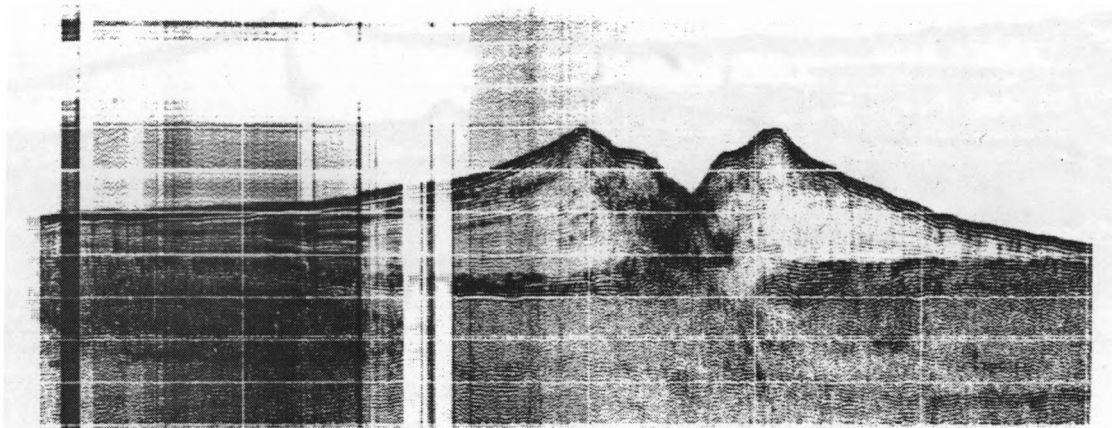


Fig. 3. Seismoacoustic profile 15.

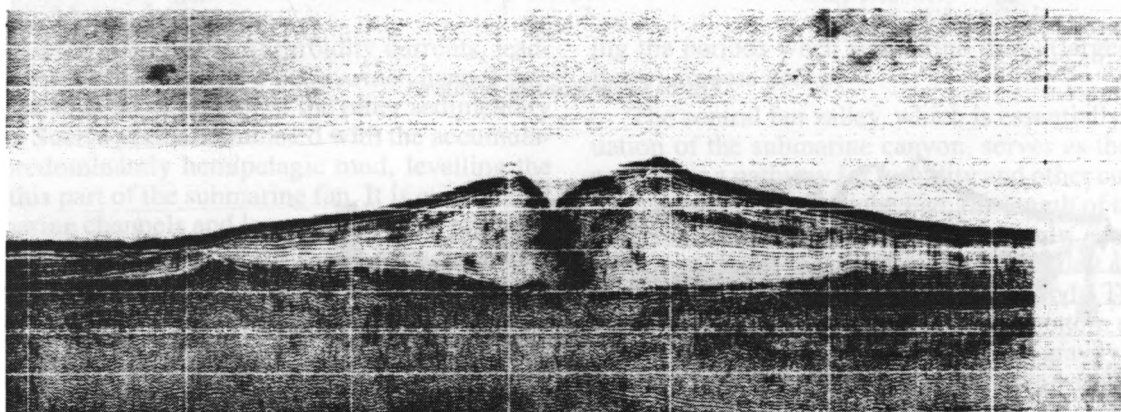


Fig. 4. Seismoacoustic profile 17.

As soon as its channel is overfilled with sediments in some areas, the river begins to excavate a new one at close range, getting around the obstructions and bending. This is also observed in the Danube Fan. For example, in profile 63, there are two erosional incisions separated by a distance of a few kilometers (Fig. 5). The southern one is rather deep and is surrounded by low levees, whereas the northern incision is not so well expressed in the seafloor relief. Its depth is likely to be no more than 60–70 m, and the width of the thalweg is no more than several tens of meters.

The conclusion that both incisions belong to the same channel is confirmed by the fact that no evidence for the presence of another active submarine valley is found in the profiles running transversely to the trend of the central accumulative rise. After making a northerly loop, the fan valley seems to break down into several relatively small submarine channels going down the northeastern slope of the central rise. In this area, that part of the deep-sea fan is located which probably can be identified as a middle fan.

(2) The middle fan. This part of the submarine fan is delimited from the abyssal side by a relatively low

but rather extended accumulative ridge which joins the central rise at an almost perpendicular direction. Its summit is cut into two parts by a valley with low levees. The depth of the valley and the height of the corresponding levees, as well as the size of the entire structure are considerably less than those of the central rise of the submarine fan. The west-facing slope of the accumulative ridge is gentler. The principal morphological elements of the seafloor (submarine channels and separating levees) north of the central rise change their sublatitudinal trend into a sublongitudinal one.

The area where the central fan valley merges with the channel, complicating the summit of the sublongitudinal marginal ridge described above, was not investigated in sufficient detail. However, it is evident that these valleys are really tied to each other. This is indicated by the presence of sand or silt layers in cores taken from the axial part of this distributary channel. Undoubtedly, even 10–12 ka ago turbidity currents transported terrigenous clastic material to this area, and this material could be supplied only from the shelf adjacent to the Danube River mouth via a system of the sub-

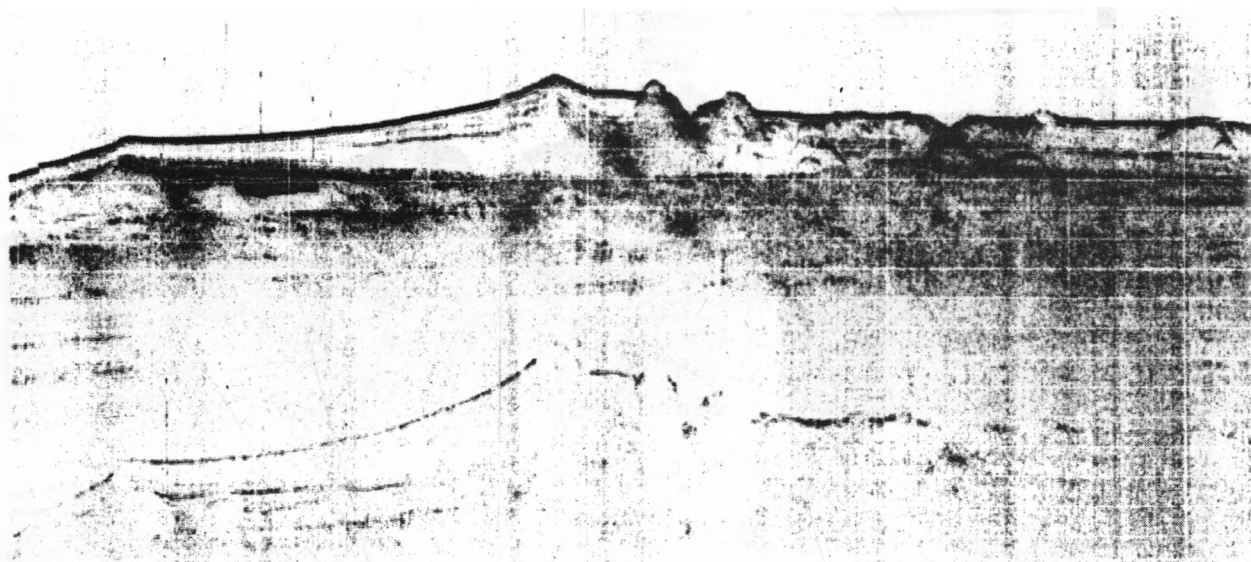


Fig. 5. Seismoacoustic profile 63.

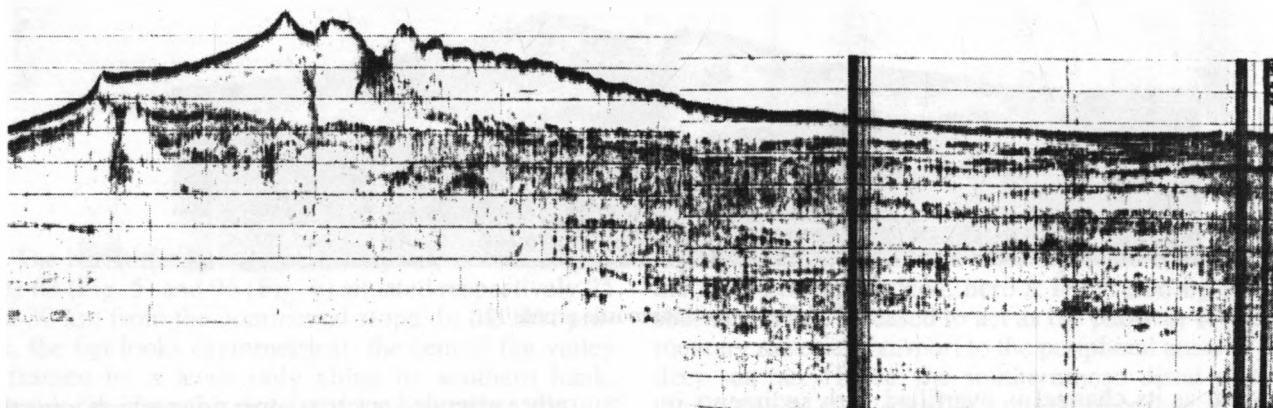


Fig. 6. Seismo-acoustic profile 96 across the upper part of the Danube fan in the turn of the central fan valley.

marine canyon—the central fan-valley—the distributary channels of the deep-sea fan.

It should be emphasized that the northwestern slope of the accumulative rise is cut in its distal part by shallow incisions that can be classified as small submarine channels and bypasses forming a branching system of the middle fan. Only some of these bypasses are bordered by levees, and their depth usually does not exceed 5–7, but is occasionally 10–15 m. While moving down the slope of the rise to the neighboring plain, the bypasses become more symmetrical in cross-section. In seismoacoustic profile 93 (Fig. 7), which was run subparallel to the main accumulative rise although slightly north of it, one can count 7 submarine channels, among which only the southernmost one is fringed by rather high levees. It probably has long presented an extension of the central fan valley.

Deep in the sedimentary sequence, one can define the outlines of one or two buried rises, having approximately the same size in cross-section as the marginal ridge delimiting the middle fan to the southeast. It is interesting that submarine channel deposits (the so-called “valley trace”) were preserved in the upper part of the buried clinoforms. The top of the buried ridge appears to be very rough and is abundant in small ledges and notches. The ridge was probably formed during the first half of the Late Pleistocene, and afterward it was buried under a cover of younger sediments. Several seismic discontinuities observed between the top of the buried rise and the seafloor are also notable for numerous irregularities. The middle, most rapidly growing part of the fan seems to have been situated for a long time in this place. Within that time interval, there were two or three periods characterized by an especially high sedimentation rate. Each of these periods

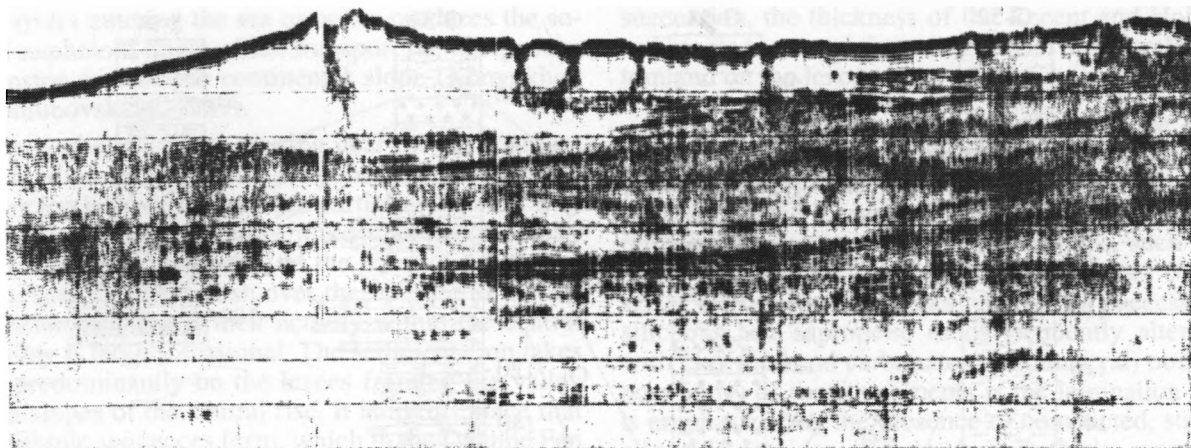


Fig. 7. Seismoacoustic profile 93 across the middle fan.

started with the activization of turbidity currents, leading to the appearance of a new submarine channel system and the erosion of the top of the older sedimentary sequence. Such a period terminated with the accumulation of predominantly hemipelagic mud, levelling the relief in this part of the submarine fan. It is evident that the submarine channels and levees constantly migrated with time within a relatively restricted area, providing a quite uniform sedimentation distribution.

At present, the boundary between the middle and the lower Danube fans is difficult to define. In order to specify its position, a detailed geomorphological survey with the use of sidescan sonars like the GLORIA or MAK is needed. This boundary is obviously situated north of the central rise because the fan prograded largely in the north direction during the Late Pleistocene. It is at this place that the branching network of small and tiny arms is situated that constitutes a distributary system supplying terrigenous material to the distal parts of the Danube Fan.

SEDIMENTARY PROCESSES AND TYPES OF SEDIMENTS ACCUMULATED IN THE DANUBE FAN

The bulk of sedimentary material is supplied to different parts of submarine fans by turbidity currents. They originate on a continental slope as a result of earthquakes or slumping and move via submarine canyons eroding their walls and bottoms. Leaving the narrow mouth of the canyon, turbidity currents move towards greater depths and spread as far as their kinetic energy admits. The turbidity current speed can reach 25–35 km/h. As the slope angle decreases, the speed retards, and part of the material that is suspended and involved in the current settles to the seafloor. The turbidity current is the main source for the formation of accumulative bodies of a fan. Another minor part of the sedimentary material comes from a water column dur-

ing the periods when submarine flows (largely gravity flows) are less active.

The central fan valley, which is essentially a continuation of the submarine canyon, serves as the channel serving as a pathway for turbidity and other currents for a long time. In the Danube Fan, the length of this valley is over 100 km. Sediments are actively accumulated mainly on the levees framing the fan valley and on the neighboring slopes of the accumulative body. The bulk of the material which accumulates on the bottom and flanks of the fan valley is eroded by subsequent gravity flows and is carried away to distal areas of the deep-sea fan.

As the turbidity currents slows down, an increasing amount of dragged and suspended material settles to the bottom, resulting in the fast sedimentary infilling of the distal part of the central fan valley. This hampers the movement of turbidity currents, and they are forced to make a new bypass. The gravity flow either breaks down into several secondary bottom currents or is deflected and forms a sort of a meander. Along the sharp turn of the valley, turbidity current, which still had a sufficient kinetic energy, is thought to have been thrown out from the channel, and the sedimentary material deposited predominantly on the adjoining slope, that is, on the northeastern slope located *en route* the channel turn due to the Coriolis force.

Thus, in the distal part of the central accumulative rise, it is the northeastern slope that became the principal depocenter. Owing to this, the slope rapidly grew and over time, was covered by a dense system of small channels and gullies.

The correlation of sedimentary cores recovered from different parts of the central accumulative rise, allowed to distinguish several main types of sedimentary sequences and to describe the most frequent facies types of sediments. It turned out that sediments which accumulated during the Pleistocene in the axial part of the central fan valley, near its walls, and on the levees are highly variable in composition and genesis (Fig. 8).

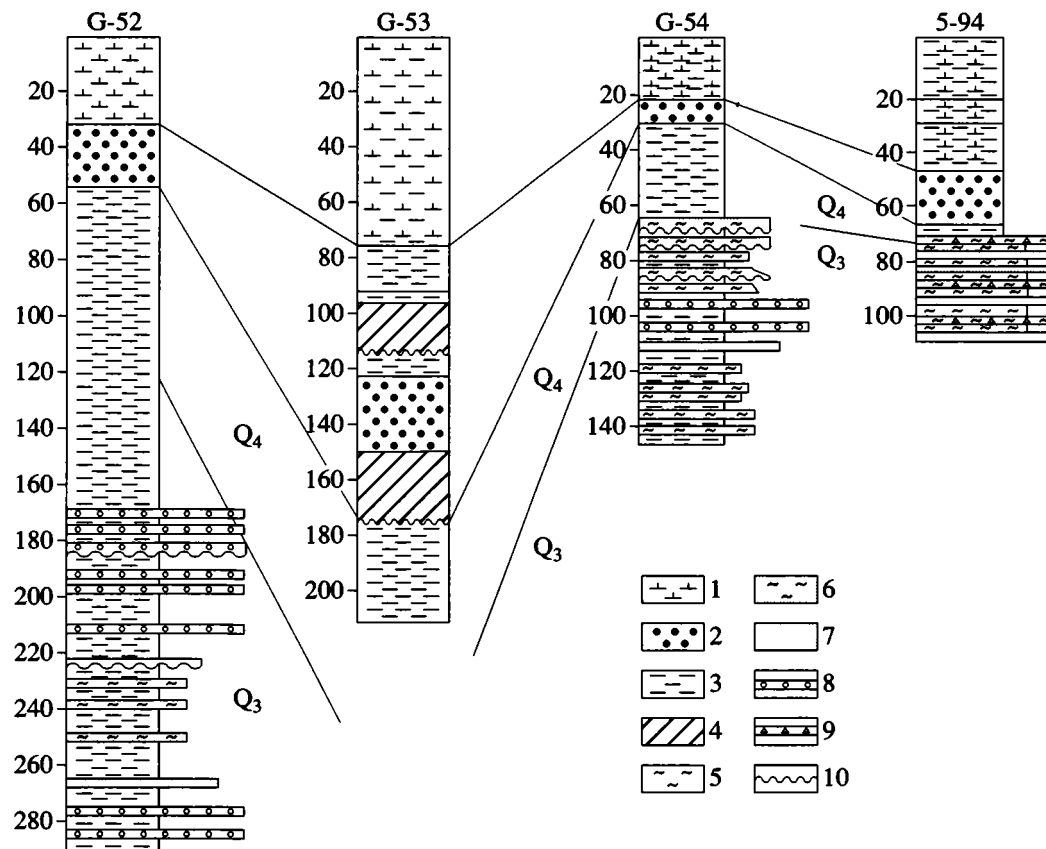


Fig. 8. Correlation of the bottom sediment cores taken in different parts of the Danube fan. Muds: (1) diatomaceous-carbonate-clay (Dzhemetin Beds), (2) sapropelic (Kalamit Beds), (3) clay, (4) slump sediments, (5) laminated sand-silt sediments, (6) sands, (7) terrigenous silts, (8) thin interbedding of silt and clay muds, (9) interlayers composed of lumps of claystones or mudstone fragments, and (10) erosion surface.

The sediments encountered on the crests of the levees stretching along the central fan valley have a rather peculiar composition. These sediments show a rhythmic pattern in the Pleistocene part of the sequence. The bases of each rhythmite, which are from 2–3 to 6–8 cm thick, are characterized by an interlayer consisting of small claystone or mudstone fragments, whose size changes from 2–3 mm to 0.5–0.8 cm. More frequently, the fragments are of gravel size. When dried out, the dark color of the fragments becomes brownish-red, testifying to the presence of hydrotroilite, which is quickly oxidized in air to iron oxides and hydroxides. This material is likely to have been eroded by submarine currents when they passed through canyons on the continental slope.

Upward the column, the clay fragments are abruptly replaced by greenish-gray clay muds. Terrigenous sands and silts are rarely observed in the described cores. They are largely found in cores taken from the peripheral part of the central rise.

The Pleistocene sediments recovered from the axial zone of the central fan valley have a completely different appearance. It should be mentioned that its deepest thalveg part has a small width (not more than 20–30 m).

This narrow axial zone is fringed by flattened terraces at an elevation of 10–15 m above the thalveg. We managed to take sediment samples directly from these areas. The Pleistocene part of these sediments is represented by frequent alternation of fine-grained sands and silts, the thickness of individual interlayers being no larger than 1–3 mm. The clay admixture is negligible. No evidence for any significant reworking is found. When dried out, the sediments become light-gray in color and massive in appearance, and their characteristic lamination becomes almost invisible. Hence, the sediments accumulated in the axial part of the fan valley are not of turbiditic origin. More likely, they are bottom current deposits. These currents went through canyons and submarine valleys during the periods of low sea-level stand.

Thus, the channel facies, whose peculiarities of distribution can be assessed from the analysis of the seismic-acoustic profiles, is characterized by fine-grained clastic sediments impoverished in clay component. The material of these sediments was transported from the shelf, more likely from the Danube Prodelta, that during the Pleistocene was situated closer to the shelf break than it is now. It is known that the discharge of

many rivers entering the sea or ocean produces the so-called nepheloid flows which transport the terrigenous suspension toward the continental slope (Konyukhov and Golubovskaya, 1989).

The nepheloid flows, moving near the seafloor, are capable of descending down canyons. Like other flows, they are loaded with terrigenous particles, which is why they are called nepheloid. Unlike classical turbidity currents, they do not spread in the form of submarine avalanches. The latter rush over the seafloor as a giant suspension cloud, and their activity within the central fan valley is largely erosional. The sedimentation takes place predominantly on the levees framing the valley and on slopes of the central rise. It is in this place that the rhythmic sequences form, which in the Danube Fan consist of mainly lumpy clays.

It must be emphasized that the deposits described above, as well as the sand-silt laminated sediments of the channel facies ceased to accumulate in the Danube Fan at the Pleistocene-Holocene boundary. This was caused by the rise of the Black Sea level resulting in a deep landward retreat of the Danube Delta. Holocene and Recent sediments of the Danube Fan do not differ from the contemporaneous sediments from other deep-water areas of the Black Sea.

At the base of the Holocene succession, there are thin light-gray muds composing the Bugaz-Vityaz Beds dated as 8–11 ka. Above, compacted, dark-brown sapropels that pass upward into water-saturated, brown-gray sapropelic muds, known as the Kalamit Beds are observed (8–3.5 ka). The very soft fluidized Dzhetmetin Beds, which are made up of the alternation of sapropelike siliceous muds with clay and carbonate coccolith sediments, are ubiquitous near the seafloor. The age of the Dzhetmetin sediments is from 0 to 3.5 ka.

The thickness of the Recent and Holocene sediments, covering the entire Danube Fan as a continuous blanket, is only 15 to 62 cm. It abruptly increases (up to 1–2 and even 5–6 m) near the walls of the central fan valley and in small depressions complicating the northeastern slope of the accumulative rise. Here, along with undisturbed sediments, there are abundant slump deposits, largely represented by Holocene sapropels with minor blueish- or greenish-gray Pleistocene clays, which normally occur among a slid mass of sapropelic sediments.

The slump genesis of the deposits described above is testified by diverse disturbances of layering, such as folding and overturning of sedimentary sequences. Mixed deposits, without any signs of layering, are often encountered. Upon being dried, they split into small lumps. Because of the numerous slumps, we failed to recover the normally lying Pleistocene sediments in the near-wall parts of the central fan valley.

Obviously, the near-wall parts of deep valleys and some depressions within the deep-sea fan are commonly filled with slumped muds. But even where slump sediments did not strongly disturb a sedimentary

succession, the thickness of the Recent and Holocene sediments is several times larger than on the valley bottom and on the levees.

Cores recovered from the place where the central fan-valley turns towards the northeast contained sediments unique. On the northern slope of the Mediterranean Ridge, the Ionian Sea, we studied similar in composition sediments in deep-water troughs, such as the Tyro and Cretheus Basins, filled with brines (Gurskii *et al.*, 1990). The sediments represent a succession of siliceous and sapropelic muds frequently alternating with clay mud and carbonate (foraminiferal) ooze. The peculiarity of these sediments is the lamination which is emphasized by the presence of compacted, structurally tied laminae, 0.3 to 1 mm thick, resembling tobacco paper sheets. During their laboratory examination, they were easily cleaved into even thinner sheets which readily rolled up. These sheetlike laminae occur among weakly compacted, water-saturated muds. They appear at a level of 2–2.5 m bsf, and their number quickly increases down the sequence.

Sediments which are very similar in composition and appearance to those described above, were found in the Danube Fan. Here, the thick sheetlike successions of siliceous-sapropelic sediments were also found. In such a succession, from top to bottom, there was observed rather a fast lithification and transformation of sediments into the structurally tied (in the bedding direction) complexes than conversion into a rock. Preliminary investigation has shown that the principal component of the laminae are variably preserved remains of silicoflagellates and diatoms cemented by weakly crystallized silica. There are structureless inclusions of organic matter and clay material as well.

It is obvious that at a depth of 2–2.5 m bsf, the redistribution of the sediment-forming components may set in within the mud sequence. As this takes place, free silica, released due to dissolution of siliceous fossils, cements individual laminae, driving out water and organic compounds into adjacent interlayers. This results in lithification of the former and liquefaction of the latter.

The large thickness of the described sediments is worthy of notice. In one of the cores, it exceeds 5 m; the sequence pattern practically does not change from top to bottom, although the ratio of siliceous, sapropelic, and other laminae strongly varies at different levels. The changes in the sediment consistency are more perceptible. Lithified section at the very bottom is composed of predominant sheetlike deposits resembling a pile of very thin paper. In the lower part of the sequence, the color of sediments becomes clearer and more contrasting: series of laminae with predominantly dark-brown or brown color alternate with laminae colored in light, greenish-green or beige hues. The former correspond in composition to clay-sapropelic muds, while the latter represent siliceous and carbonate-sili-

ceous sediments. In general, the whole sequence is rich in organic matter (C_{org} 1 to 3% TOC).

The described sediments have the Kalamit and Dzhemetin age, that is, they accumulated predominantly during the Holocene and the Recent epochs. Evidence for redeposition of the muds (slumps and other mass movement) was not found. The accumulation of such thick member of clay-carbonate-siliceous muds was probably related to specific local anomaly. It was motivated by either a high bioproductivity of surface water over the fan area or peculiarities of hydrodynamic conditions, e.g. the current vortices in water column resulting in that a large volume of organic remains and other particles suspended in water was supplied to the depression. Somehow, the accumulation rate of Holocene-Recent sediments is several times higher here than that in the neighboring areas.

Normal turbidites with terrigenous clastic material are spread, as a rule, in the middle and lower Danube fans. It is true that they were encountered here only in the Upper Pleistocene part of the sequence. At the base of the turbiditic rhythm, there is an interlayer of coarse-grained sand with gravel, often containing inclusions of small shells of mollusks or their detritus at the lowermost interval. The graded bedding in this interlayer is not always clearly displayed. Upward the rhythm, there is a frequent interbedding of sands, silts, and aleuropelites in the form of bands of 1 to 3 mm thick. They pass upward into homogeneous clay mud of blueish- or greenish-gray color, sometimes with an admixture of coarser particles at the base of this interlayer, the thickness of which can attain several centimeters. The total thickness of the single turbiditic rhythmite is within a range of 4–6 to 10–12 cm.

Incomplete rhythmites with a partially eroded upper interval of the clay mud are encountered more frequently. Sometimes the middle parts of the rhythmite are washed out as well. Within the clay muds the laminae of sand and silt are also observed, probably resulting from the activity of distributary currents with a restricted spread. The turbidites, the base of which contain different-size fragments of clay rocks (largely mudstones) rather than gravelly terrigenous sands, are quite abundant. The mudstones seem to have been washed out from the continental slope. This material is similar to that composing the upper part of the Pleistocene on the crests of the levees and on the slopes of the central rise. In this case, the lower elements of the turbiditic rhythmite have a black color that changes into rusty-brown on long contact of sediments with air because of the large content of hydrotroilite.

Upward the sequence, the lumpy clays change across a sharp contact with an interbedding of terrigenous sands and silts or a sediment with silt-sand grain size, which is made up of small clasts of old claystones and mudstones. In the latter case, almost the whole rhythmite is dark-colored. Only the interlayers of hemipelagic blueish-gray clay remain light-colored. They

were deposited during a hydrodynamically calm period separating two turbiditic events.

The terrigenous clastic sediments at the base of the turbiditic rhythmites have a small thickness, normally of 3 to 4 cm. The thicker interlayers of feldspar-quartz sands were described from only the distributary valleys of the middle Danube Fan, at the top of the Neoeuxine beds of the Late Pleistocene. An inverse-graded bedding was noted for one of these interlayers. It is of interest that in the cores taken from the neighboring submarine valleys, the terrigenous turbidite rhythmites with a rather thick interlayer of sand material at the base were found to lie at different levels of the Pleistocene sequence. For example, in one of the valleys, the turbidite with a thick sandy base was encountered among the pale-gray Bugaz-Vityaz clays. Other cores showed a complete absence of turbidites at this level of the sequence.

Obviously, different types of turbidity currents moved over different submarine valleys. Probably, two types of turbidity currents originated near the Danube Delta and Prodelta. The first one originated close to the shelf break, at the head of the submarine canyon, and transported mostly terrigenous clastic material from the delta apron. The second one, probably less powerful, originated in the canyon itself or in the adjacent areas of the continental slope, most likely as a result of slump activity. They mainly involved slope sediments—fragments of mudstones and claystones.

It is probably the second type of turbidity current that went over positive seafloor topographic features, leaving the material which formed the levees surrounding the central fan valley and the distributary channels of the fan. In this connection, it should be noted that the turbidites, which are made up of black clay fragments, sharply predominate in cores taken near mouths of the distributary channels that were probably beyond reach of material discharged by the Danube River. On the continuation of these small channels, incipient fans with main valleys and a system of distributary channels, which are much smaller than the similar valleys of the central accumulative rise, were formed. One of these tiny fans is thought to overlap the northeastern slope of the central rise, and another one is situated south of it.

CONCLUSION

Analyzing the sedimentary cores obtained from different parts of the submarine fan, one can conclude that by no means does each turbidity current leave behind its "trace" in the sequence of the central fan valley, where erosion of the valley bottom and walls rather than accumulation occurs. The bulk of terrigenous sand- and silt-sized material is carried away by turbidity currents towards the peripheral areas of the fan where they settle out. Sand and silt accumulate on the bottoms of the distributary channels, whereas clay particles deposit mainly on the levees and in the near-wall parts of the submarine channels. In this process, some

currents spread through one system of submarine channels, and others use the neighboring valleys. It is of interest that during the late Pleistocene, turbidity currents frequently moved along relic valleys. Thus, it becomes clear that the submarine fan developed non-uniformly, according to the regularities which are not yet completely known to us.

In general, with increasing distance from the continental slope, the quantity of the turbiditic rhythmites in the Late Pleistocene sequence decreases appreciably, while the completeness of individual rhythmites and their thickness increases. Meanwhile, the proportion of the layers consisting of terrigenous clastic material increases in the middle fan, gradually growing smaller toward its distant periphery. Here, sands begin to be replaced by silts, and clay interlayers play a more significant part in the rhythmite composition. Recently, accumulative bodies were discovered, such as neofans that represent areas of relatively recent and active sediment accumulation beyond the main accumulative bodies of submarine fans. Frequently, it is precisely to these neofans that the formation of thick and predominantly sand-silt sedimentary sequences is related (Nelson *et al.*, 1992; Twichell *et al.*, 1992). Similar areas have not been found in the Danube Fan.

REFERENCES

- Flood, R., Side Echoes from a Sinuous Fan Channel Obscure the Structure of Submarine Fan Channel-Levee Systems. Amazon Fan, *Geo-Marine Letters*, 1987, vol. 7, pp. 15–22.
- Gurskii, Yu.N., Konyukhov, A.I., and Burlin, Yu.K., Hydrogen Sulfide-bearing Brines and High-Mineralized Pore Water in Troughs of the Mediterranean Sea, *Dokl. Akad. Nauk SSSR*, 1990, vol. 312, no. 1, pp. 201–205.
- Konyukhov, A.I. and Golubovskaya, T.N., Sedimentation in Different Structural and Geomorphological Zones of the World Ocean, in *Itogi Nauki Tekhn., Ser. Obshch. Geol.*, Moscow: VINITI, 1989, vol. 25.
- Konyukhov, A.I. and Ivanov, M.K., Deep Structure and Sediments of the Danube Deep-Sea Fan, *Dokl. Akad. Nauk SSSR*, 1989, vol. 305, no. 1, pp. 171–175.
- Konyukhov, A.I., Ivanov, M.K., and Kul'nitskii, L.M., The Danube Deep-Sea Fan and its Sediment Facies, *Vestn. Mosk. Univ., Ser. 4: Geol.*, 1988, no. 4, pp. 28–39.
- Nelson, C.H., Twichell, D.C., Schwab, W.C., *et al.*, Late Pleistocene Turbidite Sand Beds and Chaotic Silt Beds in the Channelized Distal Outer Fan Lobes in Mississippi Fan, *Geology*, 1992, vol. 20, pp. 693–696.
- Shanmugam, G. and Moiola, R.J., Types of Submarine Fan Lobes. Models and Implications, *Am. Assoc. Petrol. Geol. Bull.*, 1991, vol. 75, pp. 156–179.
- Submarine Fans and Related Turbidite Systems*, Bouma, A.H., Normark, W.R., and Barnes, N.E., Eds., New York: Springer, 1985.
- Twichell, D.C., Schwab, W.C., Nelson, C.H., *et al.*, Characteristics of a Sandy Depositional Lobe on the Outer Mississippi Fan from Sea MARSIA Sidescan Sonar Images, *Geology*, 1992, vol. 20, pp. 689–692.

The Nature of Caspian Sea Level Fluctuations

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Abstract—In the late Cenozoic, variations of the Caspian Sea level were caused by a number of factors. At the same time, from the Early Pliocene toward the recent epoch, tectonic movements became less and less significant with time. At the recent stage, the dominating factor is the climate, and it governs the drop or rise of the basin level through its water budget.

GENERAL

The Caspian Sea level fluctuations can be followed to more or less detail beginning from the Early Pontian (Miocene) and up to the present, that is, for the last 7.0 Ma. Reconstruction of these fluctuations for the geologic past can be carried out using paleotectonic and paleogeomorphologic data using archeologic data for the middle ages of the historic time, and on the basis of instrumental observations that have been conducted since 1830. The Caspian Sea level fluctuations led, at all times, to strongly pronounced, sometimes catastrophic consequences. However, most seriously, these consequences have affected the economy of Caspian region countries during the last 60–70 years. From 1927 to 1977, the sea water area was continuously reducing up to the minimum (for the several last centuries) dimensions, necessitating the reorganization of all economic activities in the littoral zone. A dam between the Gulf of Kara Bogaz Gol and the Caspian Sea built in March 1980, allowed the slowing down of this process. Annual increments of the sea level at the expense of this measure for the period 1980–1983 were from 2 to 3 cm and the total increment was 11 cm. The water volume saved for the Caspian Sea has amounted to 41.7 km³ (Sheremet'evskaya, 1985). But the dam has also resulted in rapid deterioration of salt deposition in the classic natural self-sedimentation basin (the Gulf of Kara Bogaz Gol). Both the Gulf itself and the salt production industry connected with it, were found at the brink of extinction. Meanwhile, the sea level continued to lower. According to forecasts of 1969, the Caspian Sea level, depending on its surface discharge, would have lowered by 1.5–2 m toward 1980 (in comparison with the level of 1965), and the diversion of as much as 40 km³/year of Vichегда and Pechora waters to the south in had been planned by the end of 1980. But, quite unexpectedly, the Caspian Sea level since 1978 has begun to rise, and this had disastrous consequences, as port, irrigation, and other constructions turned out to be under water, while wind-generated flows made vast lowland pastures and other agricultural lands unsuitable for their further economic use. In the southeastern

sector of the Caspian region basin, the oil fields including the largest of them, Tengiz, were found to be under water or in the zone of wind-generated waters. Their exploitation is quite difficult due to the sea level rise which continues to the present day.

As it is known, the Caspian Sea level is almost 28 m lower than that of the World Ocean (Kholodov *et al.*, 1989). Its volume is 78 100 km³, and its area is 378 400 km². One of the most important features of the Caspian Sea is the distribution of depths. More than half of the bottom area of this sea has a depth of 100 m or less, while its southern sector is a basin (the South Caspian Basin) with depths over 1000 m. Besides, one can notice that the basin has an unusual configuration. In plan, it consists of the three parts conjugated at considerable (up to 90°) angles, the western and eastern coastal lines of every part being approximately parallel. The basin is characterized by a moderate width (196–433 km) and considerable extension (up to 1030 km). These features are due to tectonic heterogeneity of the basin bed. The northern sector of the Caspian Sea is located within the ancient East European and young Scythian–Turan platforms, whereas its southern sector enters the Alpine fold zone. Besides, according to our views, the Caspian Sea is situated within a large, submeridional rift zone.

The main rivers feeding the Caspian Sea are Volga, Kura, and Ural. The Volga accounts for 80% of the total river discharge. One of the largest waterways of the geologic past was also the pre-Amu Darya. In general, the annual inflow of river waters rises the sea level by 78 cm, the precipitation fallout by 21 cm, and the underground water inflow by 1 cm. According to estimations, evaporation lowers the sea level by 101 cm, and the discharge from the sea into the Gulf of Kara Bogaz Gol lowered the sea level by 3 cm. Therefore, prior to the dam construction, the sea level on the average, lowered annually by 4 cm. In extreme years, the sea level rise by 29 cm (1926) and drop by 34 cm (1937) was observed. On the whole, over the observation period 1925–1969, the sea level drop has amounted to 198 cm, that is, on the average, the same 4 cm per

year (Smirnova, 1974). The figures reported by Tugolesov (1948) and Zaikov (1946) are close to these. According to Zaikov, the annual negative water budget is 13.7 km^3 , and the sea level drop is 34 mm. Within the total river discharge variations, one can clearly distinguish two periods: in 1878–1936 and 1937–1977 it amounted to 331 and 272 km^3 per year, respectively. It is quite essential, as the difference reaches almost 20% (Rodionov, 1989).

The sea level rise, which began in 1978, has resulted in the fact that by 1987, its level exceeded the mark of 1977 (–29.0 m) by 1.12 m (Kosarev and Makarova, 1988, and others).

On the basis of archeologic data, it is possible to evaluate the sea level fluctuations for about 5–6 centuries. The fluctuation amplitude during this period was 5 m. In the middle of the XVI century, the sea level was at an altitude of –26.6 m, approximately 100 years later it considerably rose (up to an altitude of –23.93 m), and at the beginning of the XVIII century it again reached the minimum value of –26.0 m. The lowest (over 500 years) level was observed in 1977, when it reached an altitude of –29.0 m.

THE CASPIAN SEA LEVEL FLUCTUATIONS

According to the results of recent investigations, the present-day fluctuations of the Caspian Sea level can be explained with an accuracy to 90% by components of the water budget equation, and mainly by variations in water discharge and apparent evaporation, that is, evaporation taking into account precipitation fallout (Golitsyn and Panin, 1989; Panin and Divakov, 1991). Therefore, in the recent epoch, the volumes water budget of an unclear origin which affect the sea level fluctuations, constitute only about 10%. This value may include some neotectonic phenomena, elision processes, and so on. In this connection, the viewpoint of Academician Shilo (1989), who believes that pore waters, squeezed out from folded structures of the Caucasian region and sedimentary sequences of the Caspian syncline by tectonic stresses, enter the Caspian Sea basin, hardly seems acceptable.

The influence of climatic factors through the water budget, therefore, does not give rise to any doubt and is decisive for the explanation of Caspian Sea level fluctuations in the recent epoch. At the same time, as it will be shown below, this permanently present factor was not always a dominating one during the geologic past.

It is well known that in the Early Pontian, approximately up to the end of 6.5 Ma, the Caspian Sea communicated with the basin of Black and Mediterranean seas, and the altitudes of its level stand were governed by the World Ocean level (Chumakov *et al.*, 1992; Chumakov, 1993). The Caspian Sea, as the eastern sector of Paratethys, in that period was a basin with a much greater area in comparison with its present water area and had an indistinct shallow-water depression. The eastern

boundary of this sea reached the line Kyzyl Atrek–Nebit Dag (Fig. 1), and in the northeast, it reached the Aral Sea. Some investigators think that the Caspian and Black Sea (Euxinian) basins were separated in the second half of the Pontian age due to the beginning of Pontian Caspian Sea level drop (Andrusov, 1917; Zhizhenko, 1948; and others). Other investigators consider that the division of East Paratethys into the Caspian and Euxinian seas took place at the Early–Middle Pontian borderline (that is, 6.5 Ma ago), and the cause of this was the discharge of Pontian waters of Paratethys into the Messinian (Late Miocene) evaporative basin of Mediterranean Sea (Chumakov *et al.*, 1992). Later, in the 5.4–5.2 Ma interval (the end of Messinian), the lago–mare formation overlying salt-bearing sequence was formed in the eastern basin of the Mediterranean Sea; this formation is known only here and has the fauna of molluscs and ostracodes, inherent to the Pontian Paratethys (Chumakov *et al.*, 1992). In our opinion, the Caspian and Euxinian seas were separated due to two reasons: first, the discharge of Paratethys waters and, second, the appearance of a cofferdam along the line Stavropol' Arch–Mineral'nye Vody Spur of the Central Caucasus. This anticaucaasian structure has been known at least since the Late Jurassic, when it separated the East Ciscaucasian and West Ciscaucasian evaporite subbasins (Baikov *et al.*, 1987).

In the Middle–Late Pontian (Shemakha and Babadzhan time) no essential drop of the Caspian Sea level occurred. Chumakov *et al.* (1992) believe that this process started only at the end of Babadzhan time (the latest Miocene–earliest Pliocene).

Two important events marked the borderline Miocene–Pliocene and the beginning of Early Pliocene.¹ The Gibraltar “slit” opened in the west of Mediterranean region, and therefore the World Ocean, Mediterranean Sea, and Euxinian Basin instantaneously (from the geologic standpoint) leveled off, but the latter failed to merge with the Caspian Sea. On the contrary, an extremely strong and abrupt drop of the Caspian Sea level occurred in the Balakhan time due to the intensive and sedimentation-uncompensated subsidence of the South Caspian Depression, as well as the closely associated South Turkmenian Depression (Yanshin, 1953; Luppov, 1963; Milanovskii, 1963; Bliskavka, 1963; Garetskii and Yurevich, 1964; and others). Judging from the depth of river thalwegs, that fed the Balakhan (Early Pliocene) Caspian Basin, its level was at altitudes –500 ... –600 m and lower. In our opinion, activation of the Caspian rift, especially the South Caspian Depression, whose depth was rapidly

¹ Formerly the Pliocene Epoch in this region was divided into three ages and now it is divided into only two ages. To avoid misunderstanding, we therefore use in the following text the term “Balakhan time.” It corresponds to the Middle Pliocene of the previous scale (Yanshin, 1953; Luppov, 1963; Milanovskii, 1963; Kvasov, 1977; and others) and to the Early Pliocene of the modern geochronologic scale for the Late Cenozoic of Mediterranean and Paratethys basins (Nevesskaya *et al.*, 1984; Chumakov *et al.*, 1992).

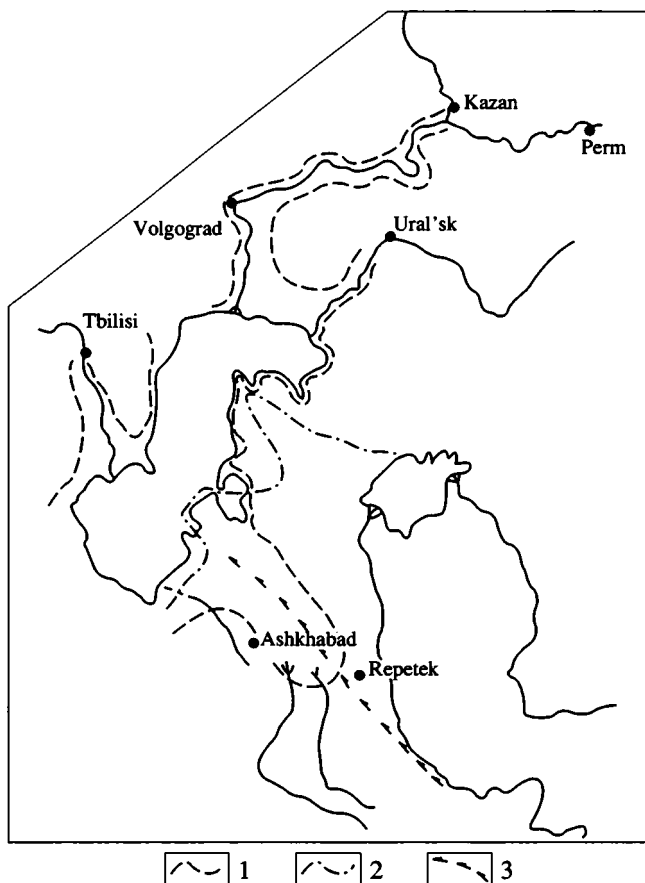


Fig. 1. Extension of the Akchagyl transgression. (1) Boundary of the Akchagyl basin; (2) eastern boundary of the Ponto-Caspian basin in Turkmenistan and Aral region; (3) the Early Pliocene (Balakhan) erosional valley of the pre-Amu Darya.

increasing, is related to this period. Abrupt drop of the erosion base level resulted in the development of a branched system of very deep erosional entrenchments. These are unique formations; so are still deeper erosional incisions of paleorivers related to the Messinian age of the Mediterranean Sea, which is a basin of the intercontinental type (Chumakov, 1967; and others). Very deep, now buried valleys of the Amy Darya, Volga, Emba, and Ural paleorivers, the rivers belonging to the Caucasian coast of the Caspian Sea and their tributaries originated (Belenitskaya and Sedletsii, 1982; and others). In the Balakhan time, a powerful drainage system was formed, and it brought about the manifestation of erosional karstic cycle everywhere throughout the Caspian Basin. The cycle was especially widespread in the territories, where the system of paleoincisions was developing after readily soluble halogenous-sulfate and carbonate deposits. The ancient erosional karstic systems of Turkmenistan are the most studied, as extensive drilling operations connected with the prospecting for oil and gas had been conducted there. The valleys of paleorivers have a similar structure. Their width usually does not exceed 7–10 km, the inci-

sion depth is up to altitudes –400 ... –600 m and more. These valleys are made up by the Lower Pliocene (Balakhan) alluvial and younger deposits, whose total thickness is as much as 800 m (Fig. 2). At the western coast of the sea, a very deep valley can be followed approximately to Tbilisi, and in the north a similar valley can be followed along the Volga valley to Kazan. It should be noted that the Early Pliocene valleys were formed not only along the main waterway but also practically along the whole river system including all tributaries.

In the period of catastrophic drop of the Caspian Basin level, its dimensions were reduced to those of the South Caspian Depression with the adjoining West Turkmenian Depression. The depressions became the arena of extraordinarily intensive sedimentation, where the drainage system carried from all directions enormous masses of sedimentary material. The deltas of paleo-Volga and paleo-Amu Darya rivers virtually closed up with each other, forming a powerful, more than 3000 m thick, body of deltaic deposits that later became productive petroliferous sequences of the Apsheron and Cheleken formations. The depth of the South Caspian Depression, judging by the thickness of the Lower Pliocene deposits reached at this stage its maximum values and possibly exceeded 4000 m. The described processes undoubtedly led to rapid uncompensated filling of the basin with the Lower Pliocene deposits. As a result of this, the basin volume during the short time interval started to decrease rapidly, causing the closure of erosional entrenchments, their filling with sediments, reduction of the South Caspian Depression depths, and subsequent Akchagyl transgression. As it has been noted, in the Balakhan time at present-day climate, the alluvium supply into the Caspian Sea was equal to 0.21 km³ per year and 210000 km³ in one Ma; this volume is equivalent to a thickness of the productive sequence of an order of 1100 m over the whole basin area (Kvasov, 1966). If now the South Caspian Depression area within the isobath of 500 m is about 55000 km², then in the Pliocene, according to Kvasov, it reached 200000 km² at the expense of the adjacent West Turkmenian and Kura depressions. One should keep in mind that the volume of water in the modern Caspian Sea is 78100 km³.

The Upper Pliocene marine brackish-water deposits of the Akchagyl age (the lower boundary is 3.4 Ma, according to Chumakov *et al.*, 1992), transgressively overlying the Lower Pliocene and older formations, allow us to outline in detail the Akchagyl basin water area (Fig. 1). This basin with the area not less than 900000 km² considerably exceeded the modern water area of the Caspian Sea. In the north, it extended along paleoentrenchments up to Kazan, in the south, up to Tbilisi, in the east, up to Repetek (the Southeast Kara Kum). Maximum altitudes of the Akchagyl time sea reached +125 m (Kvasov, 1977). The thickness of Akchagyl marine deposits in West Turkmenistan is 400 m and more (*Geologiya SSSR*, 1972).

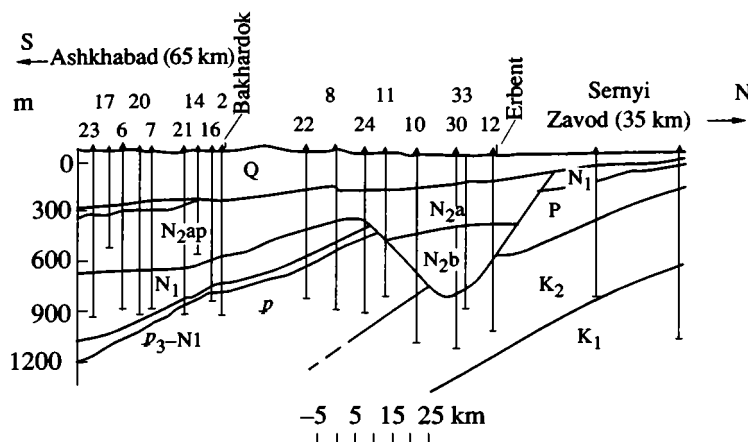


Fig. 2. The Early Pliocene (Balakhan) section of the pre-Amu Darya in the western sector of Turkmenistan (Bliskavka, 1963). Numbers 23, 17, etc. denote the drilled boreholes. Rock age: (K₁) Early Cretaceous, (K₂) Late Cretaceous, (P) Paleogene, (P₃-N₁) Late Paleogene-Early Miocene, (N₂b) Balakhan deposits, (N₂a) Akchagyl, (N₂ap) Apsheron deposits, (Q) Quaternary formations.

According to notions that were widespread not long ago, the Akchagyl basin was not connected with the Black Sea, and its level was not governed by the ocean level (Kvasov, 1977; Nevesskaya *et al.*, 1984; and others). Only during a very short period it was connected by a narrow strait with the basin of the North Black Sea region. The Taman Horizon with obviously late Akchagyl fauna has long been known in Azov-Kuban Depression; i.e., the Akchagyl basin was by the end of its existence connected with the Black Sea region (Zhizhchenko *et al.*, 1968). Nevesskaya *et al.* (1984) suppose that the penetration of waters from the Akchagyl sea far to the west was a short-term episode that probably coincided with the maximum (or two maxima) of transgression. The character of contact between the Lower Pliocene and Akchagyl deposits does not bear any noticeable signs of washout, which evidently points to an extremely rapid rise of water level in the Akchagyl basin. The maximum of transgression is related to the Middle Akchagyl stage. It should be also noted that the water of this basin was relatively saline. The subsequent rapid transgression of the Late Akchagyl sea was accompanied by their intensive desalination.

Chumakov *et al.* (1992) consider that the Akchagyl transgression of the Caspian Sea is connected with the corresponding transgression of the World Ocean that spreaded through the Mediterranean Sea to the Euxinian (Black Sea) Basin and then to the Caspian Basin. Previously many investigators, in particular Yanshin (1953), explained the Akchagyl transgression by a breakthrough of oceanic waters into the Caspian Basin, though the paths of such a breakthrough had not been found. The oceanic transgression resulted in the fact that in the Akchagyl time the Euxinian and Caspian seas were united into a common basin. The undisputable proof of this transgression is the presence of calcareous nannoplankton considered as an evidence of the link between the above basins and the World Ocean. However the nannoplankton complexes, at least in sur-

face sections, as Chumakov *et al.* (1992) point out, have been encountered only in very narrow time intervals or even in a single sample.

In our opinion, the findings of nannoplankton and other facts mentioned above allow us to draw the following conclusions. In the Akchagyl age, the link between the Caspian and Euxinian seas was only periodical but repeated, when the breakthrough of a cofferdam along the line Stavropol Arch-Central Caucasus took place. The rapid supply of marine water from the Euxinian Sea, overflow of Caspian water into the Azov-Kuban depression region or termination of the discharge certainly promoted the Akchagyl transgressions and the Caspian Sea regressions. Probably for this reason, the salinity of water in this sea considerably increased in transgressive epochs and decreased in regressive ones.

In the post-Akchagyl time, during the Apsheron age, one more moderate transgression of the Caspian Sea has been geologically documented. Its scale is uncomparable to that of the preceding Akchagyl transgression. Thus, in Turkmenistan, the Apsheron sea spread across the territory of West Turkmenistan Lowland, surrounded the Bol'shoi Balakhan and penetrated into the Kara Kum Lowland somewhat eastward from the Kyzyl-Arvat meridian. The reason for this transgression remains unclear. On the basis of nannoplankton findings in the Apsheron deposits (Semenenko and Lyul'eva, 1978), Chumakov (1993) has supposed that this transgression, like the Akchagyl one, was caused by the World Ocean level variations.

The history of Caspian Sea in the post-Apsheron time is marked by a number of well-known transgressions. The Baku, Khazar, and Khvalyn transgressions are most significant of them. During the most extensive Khvalyn transgression the sea-level rose almost by 80 m above its present-day level (up to altitudes of 47-49 m), and the area of sea water area reached

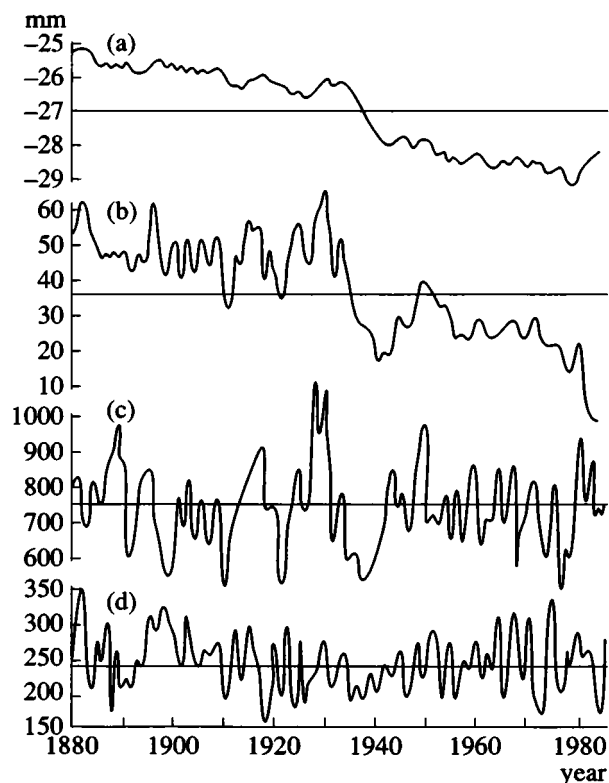


Fig. 3. Curves of fluctuations in (a) the Caspian Sea level; (b) the Kara Bogaz Gol level; (c) the river waters influx into the sea; (d) the amount of precipitation fallout (Shilo, 1989).

950000 km². It should be noted that at this stage, the short-term communication of the Caspian and Black Sea basins was established through the Kuma–Manych depression. In this period, tectonic movements in the considered territory were quite intensive, as before. At the end of Middle and beginning of Late Pleistocene, a significant turn of the Amu Darya discharge from the latitudinal to northwest direction took place. The reason for this turn, in our opinion, was the formation of a tectonic arch—a cofferdam between the Central Kara Kum arch and the Kopet Dag. Simultaneously with this, development of the Stavropol Arch resulted in termination of the discharge through the Kuma–Manych Depression, and the newly formed cofferdam finally separated the catchment basins of Caspian and Black seas.

The vast region including the Caspian Sea water area and the Caspian Depression has exhibited until recently a strongly pronounced tendency towards steady subsidence. Tectonic dynamism of the Caspian Sea region, in our opinion, can be attributed to the large rift which exists there and was intensely developing in the Alpine time. Downward movements, obviously dominating over a long period, have resulted in the accumulation of the powerful, more than 20 km thick sequence of sedimentary rocks in the Caspian and South Caspian depressions. Suffice it to note that the thickness of the

productive Apsheron formation alone exceeds 300 m. The evidence of subsidence is the abrasional bench, worked out in the Akchagyl deposits, that skirts the eastern coast of Caspian Sea (Vdovikin, 1990). The recurring sea level rise looks especially unexpected against this background and needs to be explained. As it was already mentioned, these level fluctuations seem an integral reflection of the effect of a number of factors. The most common explanation of the Caspian Sea level fluctuations in the historic time is the viewpoint of climatologists and hydrologists on a complete correlation of this process with variations in climate and water budget. One cannot but agree with this, but, however, with certain reservations. As it is seen from Fig. 3, variations in the river discharge and precipitation fallout are not fully correlated with those in the levels of Caspian Sea and Gulf of Kara Bogaz Gol. Disturbance in this correlation has been observed since 1937, that is, from the moment of appreciable drop of the Caspian Sea level. The above-mentioned estimations of Zaikov, Radionov, and other investigators also point to a noticeable lack of coincidence between the water budget estimations and the actually observed phenomena. However, it should be noted once again that for the historic period one of the predominating factors is climatic. Many researchers try to explain the catastrophic Early Pliocene regression of the Caspian Sea as well from the standpoint of the leading role of the climatic factor, according to the method of actualism (Tugolesov, 1948; and others). But for this purpose, it is necessary to take high important hypothetic assumptions. Thus, for example, according to Kvasov (1977), the Volga Basin in its middle sector (upstream Kazan) might have been barred by a highland, and a considerable portion of the discharge was delivered not into the Caspian Basin, but northward. To explain the Akchagyl and Apsheron transgressions, this author assumes the existence of glaciers in the northern sector of present-day Barents Sea (the Barents glacial shield). They barred off the discharge of northern rivers, and the latter were compelled to turn southward. The Khvalyn transgression is related to the appearance of glaciers stretching from the Valdai Highland to the Urals. The glaciers also barred off the discharge in the northern direction and caused the glacial lakes to discharge their waters southward into the Volga basin. However, the available facts indicate, as Kaplin *et al.* (1977) have shown, that the sea level fluctuations can be quite far from any coincidence with glacial epochs, at least for the Quaternary period (Fig. 4). Tugolesov (1948) has noted that the influx of all marine water into the South Caspian Depression could be attributed solely to the climatic factor. However, the extrapolation of modern climatic data to the Early Pliocene epoch is only an assumption. Luppov (1963) has supposed that the cause for the Akchagyl transgression, along with climatic processes (cooling and humidification of climate), was an intensive elevation of the South Caspian Depression bottom. Chumakov *et al.* (1992), as was mentioned above, con-

nect the Akchagyl transgression (through the Euxinian and Mediterranean seas) with the World Ocean level fluctuations.

Some investigators explain the pulsational character of variations in the Caspian Sea level by the Sun–Earth and Moon relations; they believe that these relations cause cyclic climate variations and affect lithospheric dynamics, which manifests itself in neotectonic movements (Smirnova, 1974; Leont'ev, 1988; Vdovykin, 1990). Thus, the data of Vdovykin (1990), revealing the correlation of sea level fluctuations with solar activity, are plotted in Fig. 5. It is interesting that Smirnova (1974) predicted the present-day rise of the Caspian Sea level, which coincided in time with the real progress of this process. However, the doubtless predomination of climatic factor in the recent epoch makes any forecasts for the nearest perspective fairly unreliable, since a theory of prediction of climatic conditions for the 30–50 year perspective is not available at present.

Further, we should dwell on the explanations of Caspian Sea level fluctuations proposed by Naidenov and Kozhevnikova (1994), who used the ideas and methods of synergetics and the modern theory of stochastic (random) processes. These investigators suppose that a physical mechanism retarding the Caspian Sea response to any change of climatic situation exists. Since the laws of evaporation from the surface of deep and shallow seas are different, the hydraulic budget equation for the second case becomes essentially nonlinear. The authors built the nonlinear discrete model of Caspian Sea level fluctuations, and on its base performed their calculations that revealed the following.

The sea level regime is characterized by prolonged periods (200–400 years) of the stand around stable equilibrium states and rapid transitions (20–40 years) from one level to another. The locally stable equilibrium states have altitudes of –25.4 m and –27.9 m; the absolutely unstable state has an altitude of –26.4 m. The sea, having passed the altitude –26.4 m, becomes already practically incapable of returning to the initial equilibrium position, the lower equilibrium level being less stable than the upper one. The next years will be decisive. According to Naidenov and Kozhevnikova (1994), if the sea level passes the unstable altitude –26.4 m, the probability of its transition to a higher level will grow exponentially. It should be pointed out that by the end of 1992 the Caspian Sea level rose to an altitude of –27.05 m.

The proposed model contains an important component of a forecast: a sufficiently high probability of rise or drop of the Caspian Sea level always exists. It allows us to understand why any forecasts concerning the Caspian Sea level fluctuations have not proven to be correct. Since the stable regime levels are close to each other, the sea often slips down to the unstable region of variations, which usually confuses any forecast.

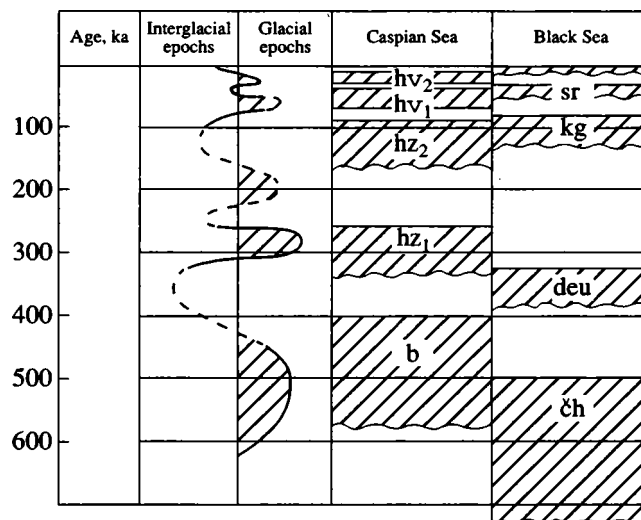


Fig. 4. Caspian Sea and Black Sea transgressions versus glacial epochs in the East European Plain (Kaplin *et al.*, 1977). Transgressions: (b) Baku; (hz₁) Early Khazar; (hz₂) Late Khazar; (hv₁) Early Khvalyn; (hv₂) Late Khvalyn; (ch) Chaudin; (deu) ancient Euxinian; (kg) Karangat; (sr) Surozh.

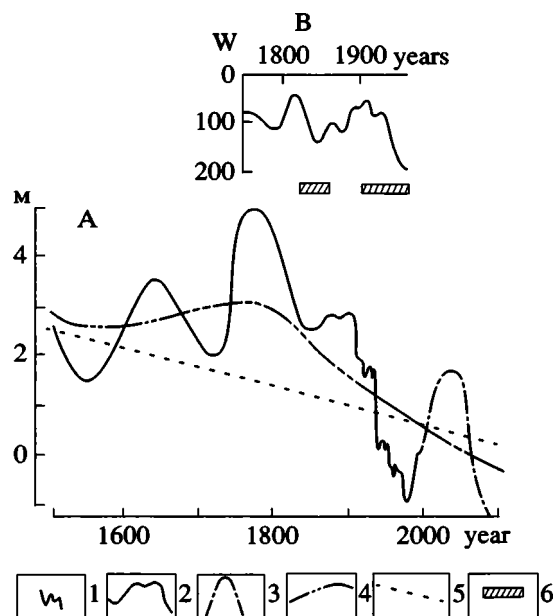


Fig. 5. The curve of relative variations of the Caspian Sea level during the retrospective and predicted periods (A) and the solar activity curve as a function of the relative Wolf numbers, W (B) (Vdovykin, 1990). Cycle numbers: (1) 11-year; (2) secular; (3) predicted; (4) segment of the 800-year macrocycle; (5) general trend of neotectonic subsidence; (6) curve segments correlating with the curve of Caspian Sea level variations.

The existence of two metastable, weakly steady equilibrium levels, separated by a region of instability, makes the Caspian Sea behavior essentially unpredictable. But theoretically, it is possible to stabilize the sea

level near one of the stable altitudes, the upper or lower one. For this purpose, it is necessary to take away (or add) a certain volume (layer) of water, so as to return the sea into the zone, where the higher or lower regime exists. This volume is approximately equal to 1000 km³, that is, the water volume between the upper and lower levels.

In conclusion, Naidenov and Kozhevnikova write the following. *The Caspian Sea ... being put out from the stable equilibrium by the extraordinary shallowing of the Volga River in the 1930s and not long having stayed at an altitude of -28.3 m, at present is relaxing to its more stable upper level. If in the nearest years the Caspian Sea passes the unstable level (-26.4 m), then the greater probability of the sea level stabilization at an altitude of -25.5 m will appear* (Naidenov and Kozhevnikova, 1994, p. 12).

Analyzing the amplitude and duration of the Caspian Sea transgressions (Fig. 4) and taking into account the Early Pliocene and Apsheron stages, one cannot but note a clearly pronounced relationship. The scale of transgressions and regressions and their duration decrease from the Early Pliocene toward the Holocene. Against this background, the frequency of pulsations grows. Therefore, the combined affect of a number of factors causing the Caspian Sea level variations becomes weaker over the course of time, and the sharp variations of the past are replaced at the recent stage by the regime of minor fluctuations.

CONCLUSION

The foregoing facts allow us to arrive at the following conclusions:

(1) The Caspian Sea during the pre-Middle Pontian time represented a relatively shallow-water basin, whose level was governed by the World Ocean level, and the united system of inland (Mediterranean, Black, and Caspian) seas evidently broke down only in the Late Miocene, at the borderline of 6.3–6.5 Ma, when evaporitized sediments and then salts of the Messinian time began to deposit in the Mediterranean Sea.

(2) The catastrophic drop of the Caspian Sea level during the Early Pliocene is connected with an abrupt deepening of the South Caspian Depression due to riftogenesis processes. The adjacent territory (large West Turkmenian Depression) was also involved into deep subsidence. The manifestation of a very large karstic erosional cycle, which covered vast spaces of Central Asia, Ciscaucasia, and northern sector of the Caspian Sea basin, occurred as a result of the sharp sea level drop down to altitudes of -600 m and less. The climatic factor effect in this period was subordinate against the background of the dominating tectonic factor.

(3) The drift of sedimentary material along the system of erosional entrenchments in the Early Pliocene resulted in the development of avalanche terrigenous sedimentation, formation of the thick sequence of deltaic petroliferous deposits, first of all, in the pre-Volga

and pre-Amu Darya river basins, as well as in the partial sedimentation-compensation of the South Caspian Depression and filling of the West Turkmenian Depression with sediments. The very extensive Akchagyl transgression appeared as a consequence of this, as well as of a periodic breakthrough of waters from the Mediterranean Basin freely communicating with the World Ocean, and probably a rise of the South Caspian Depression bottom. The Akchagyl transgression is subdivided into three stages, the Middle Akchagyl stage being the largest of them. The scale of manifestations of the Akchagyl transgressions and regressions is unlikely to depend on superimposition of the climatic factor. Salination of the Akchagyl basin water in periods of transgressions, and its desalination during regressions, observed from the character of deposits, rule out the dominating role of the climatic factor.

(4) The subsequent transgressions, beginning from the Apsheron one, were of a local character and could be equally caused by the effect of both climatic and neotectonic factors. In this case, the activity of neotectonic movements is confirmed by the change of the Amu Darya flow direction, closure of the Kuma–Manych Strait, and other geologic factors.

(5) In the Quaternary period, the Caspian Sea level variations did not always correlate with glacial epochs, which points to the substantial influence of neotectonic movements.

(6) In historic time, the leading role in the Caspian Sea level fluctuations is switched over to the climatic factor. At the same time, the water budget estimations cannot exhaustively explain the observed pulsations of its level, and the effect of neotectonics, as a minor factor, can be evaluated approximately as 10% of the real sea level variation.

(7) On the whole, the history of transgressions and regressions of the Late Cenozoic Caspian Sea, as a basin isolated both completely and partially, begins from the Middle Pontian stage. The first, very extensive regression occurred in the Early Pliocene, when, in our opinion, the South Caspian rift depression was sharply activated. Since then and until the recent stage, the amplitude, scale, and duration of transgressions and regressions decrease, and the frequency of their manifestation in time grows. The whole Caspian Basin system, therefore, arrives at the tectonically balanced state. The tectonic factor resulting in most catastrophic changes becomes less and less effective. The leading role in the sea level fluctuations is transferred to the climatic factor which however, is unable to cause events comparable in their scale with those occurring in the geologic past.

The materials presented in this article should be considered as one of the attempts to generalize the observed phenomena and calculated data. A reliable forecast of the Caspian Sea level variation can be obtained on the base of analyzing the whole history of the Caspian Sea Basin, taking into account the completeness of all factors.

REFERENCES

- Andrusov, N.I., The Pontian Stage, in *Geologiya Rossii* (Geology of Russia), Petrograd: Geolkom, 1917, vol. 4, part 2, issue 2.
- Baikov, A.A., Sedletsii, V.I., and Semenov, G.A., The Upper Jurassic Evaporate Formation and Block Tectonics in the Northern Caucasus, *Litol. Polezn. Iskop.*, 1987, no. 2, pp. 95–111.
- Belenitskaya, G.A. and Sedletsii, V.I., The Late Neogene–Quaternary Erosional Karstic Cycle in the Caspian Sea Basin, with the Central Asia and Ciscaucasia as Example, *Litol. Polezn. Iskop.*, 1982, no. 4, pp. 117–123.
- Bliskavka, A.G., The Erbent Erosional Section, in *Novye Dannye po geologii zapadnoi chasti Srednei Azii. Problemy neftenosti v Tsentral'noi Azii* (New Data on the Geology of Western Central Asia: The Problem of Oil-Potential in Central Asia), Leningrad: Gostoptekhizdat, 1963, pp. 38–43.
- Chumakov, I.S., *The Pliocene and Pleistocene Deposits of the Nile Valley in Nubia and Upper Egypt*, Moscow: Nauka, 1967.
- Chumakov, I.S., Byzova, S.L., and Ganzei, S.S., *Geokhronologiya i korrelyatsiya pozdnego kainozoya Paratetisa* (Geochronology and Correlation of the Late Cenozoic of Paratethys), Moscow: Nauka, 1992.
- Chumakov, I.S., The Radiometric Scale of the Late Cenozoic of Paratethys, *Priroda*, 1993, no. 12, pp. 68–75.
- Garetskii, R.G. and Yurevich, A.L., The Problem of the Origin of Repetek and Bairamali Zones of Salt Anticlines in Southeast Turkmenistan, *Dokl. Akad. Nauk SSSR, Ser. Geol.*, 1964, vol. 158, no. 3, pp. 598–601.
- Geologiya SSSR* (Geology of the USSR), Geologic Description, Moscow: Nauka, 1972, vol. 22.
- Golitsyn, G.S. and Panin, G.N., On the Water Budget and Recent Fluctuations of the Caspian Sea Level, *Meteorol. Gidrol.*, 1989, no. 1, pp. 57–64.
- Kaplin, P.A., Leont'ev, O.V., Rychagov, G.I., Parunin, O.B., Svitoch, A.A., and Shlyukov, A.I., Chronology and Paleogeography of the Ponto-Caspian Sea in the Pleistocene (based on the Absolute Dating), in *Paleografiya i otlozheniya pleistotsena yuzhnykh morei SSSR* (Paleogeography and Deposits of the Pleistocene in Southern Seas of the USSR), Moscow: Nauka, 1977, pp. 33–42.
- Kholodov, V.N., Khrustalev, Yu.P., Lubchenko, I.Yu., et al., *Kaspiiskoe more. Problemy sedimentogeneza* (The Caspian Sea: The Problems of Sedimentogenesis), Moscow: Nauka, 1989.
- Kosarev, A.N. and Makarova, R.E., Fluctuations of the Caspian Sea Level and the Possibility of Their Prediction, *Vestn. Mosk. Univ., Ser. 5: Geogr.*, 1988, no. 1, pp. 21–26.
- Kvasov, D.D., The Water Budget of Caspian Sea in the Middle Pliocene, *Byull. Mosk. O-va Ispyt. Priro. Otd. Geol.*, 1966, no. 6, pp. 99–114.
- Kvasov, D.D., The Causes for Transgression of the Caspian and Black Seas During the Pliocene and Quaternary, in *Paleografiya i otlozheniya pleistotsena yuzhnykh morei SSSR* (Paleogeography and Deposits of the Pleistocene in Southern Seas of the USSR), Moscow: Nauka, 1977, pp. 17–24.
- Leont'ev, O.K., The Problem of Caspian Sea Level and the Stability of Caspian Sea Coasts, *Vestn. Mosk. Univ., Ser. 5: Geogr.*, 1988, no. 1, pp. 14–20.
- Luppov, N.P., The Middle Pliocene Stage in Geologic History of the Transcaspien Region, in *Novye Dannye po geologii zapadnoi chasti Srednei Azii. Problema neftenosti Srednei Azii* (New Data on the Geology of Western Central Asia: The Problem of Oil-Potential in Central Asia), Leningrad: Gostoptekhizdat, 1963, pp. 11–37.
- Milanovskii, E.E., The Paleogeography of Caspian Basin During the Middle and Beginning of the Late Pliocene, *Byull. Mosk. O-va Ispyt. Priro. Otd. Geol.*, 1963, vol. 38, issue 3.
- Naidenov, V.I. and Kozhevnikova, I.A., Is the Sea Level Predictable?, *Priroda*, 1994, no. 5, pp. 4–12.
- Neveeskaya, L.A., Voronina, A.A., Goncharova, I.A., Il'ina, L.B., Paramonova, N.P., Popov, S.V., Chapalyga, A.L., and Babak, E.V., The History of Paratethys, *Dokl. 27 sessii MGK* (Reports 27 Session IGC), *Paleoceanology*, Moscow: Nauka, 1984, pp. 91–101, vol. 3.
- Panin, G.N. and Divakov, I.V., The Evaluation of Possible Variations of Evaporation in the Northern Caspian Sea During the Sea Level Rise, *Meteorol. Gidrol.*, 1991, no. 5, pp. 62–68.
- Rodionov, S.N., Climatic Analysis of the Extraordinary Rise of the Caspian Sea Level in the Recent Years, *Izv. Akad. Nauk SSSR, Ser. Geogr.*, 1989, no. 2, pp. 73–81.
- Semenenko, V.N. and Lyul'eva, S.A., The Experiment of Direct Correlation between the Miocene–Pliocene of East Paratethys and Tethys, in *Stratigrafiya kainozoya Severnogo Prichernomor'ya i Kryma* (Stratigraphy of the Cenozoic in the Northern Black Sea Region and the Crimea), Dnepropetrovsk: Dnepropetr. Univ., 1978, issue 2, pp. 95–105.
- Sheremet'evskaya, O.I., Improvement of a Method for Predicting the Annual Variation in the Caspian Sea Level, *Meteorol. Gidrol.*, 1985, no. 4, pp. 67–71.
- Shilo, N.A., The Nature of Caspian Sea Level Fluctuations, *Dokl. Akad. Nauk SSSR, Ser. Geol.*, 1989, vol. 305, no. 2, pp. 412–416.
- Smirnova, K.I., The Regime of Recent Caspian Sea Level and the Its Prediction in Future, *Meteorol. Gidrol.*, 1974, no. 1, pp. 56–61.
- Tugolesov, D.A., The Causes for Transgressions and Regressions of the Caspian Sea, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1948, no. 6, pp. 131–140.
- Vdovykin, G.P., The Relation between Caspian Sea Level Fluctuations and Neotectonic Movements, *Dokl. Akad. Nauk SSSR, Ser. Geol.*, 1990, vol. 310, no. 3, pp. 673–675.
- Yanshin, A.L., Geology of the Northern Aral Sea Region: Stratigraphy and History of Geologic Development, *Mater. Poznan. Geol. Stroen. SSSR, Nov. Ser.*, 1953, issue 15(19).
- Zaikov, B.D., The Water Budget of Caspian Sea in Connection with the Factors of Its Level Drop, *Tr. Nauch. Issled. Uchrezhd. Gidrometsluzhby USSR*, 1946, ser. 4, issue 38.
- Zhizhenko, B.P., The Evolution History of Basins in the Euxinian–Caspian Region during the Pliocene, *Byull. Mosk. O-va Ispyt. Priro. Otd. Geol.*, 1948, vol. 23, issue 1.
- Zhizhenko, B.P., Serezhchenko, V.A., and Churilova, E.V., The Pliocene in *Geologiya SSSR* (Geology of the USSR) Moscow: Nedra, 1968, vol. 9, part 1, pp. 426–441.

Biochemogenic Formation of Phyllosilicates during Hydrothermal Alteration of Basalts in Iceland

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Abstract—In the course of optical and electron-microscopic investigations, the following frequently encountered formations were noted within cavities and fissures in basalts: (1) rims on the gas vesicle walls; (2) so-called “sedimentation levels” (which resemble in structure sediments accumulated in various-type settlers, where series of horizontally layered deposits are formed); (3) branching and sometimes felted “threads”; (4) vermicular offshoots on surfaces of the rims and of the sedimentation level-type formations; (5) globules of various dimensions and globule intergrowth clusters, sometimes similar in form to a bunch of grapes; and (6) intricate reniform aggregates, consisting of individual spherical and oval bodies.

The structural features of the biomorphic aggregates, as well as the character of their interrelations with host rocks and the paragenetic complex of secondary minerals, allow one to consider these formations to be a result of bacterial action on the mineral-forming environment, causing the development (within a microvolume) of conditions that are favorable for concentration of the elements required for the generation of the smectite–celadonite mineral complex.

In Iceland, within the upper temperature zone of the altered basalts, green-colored clay minerals are widespread. Among them, smectites are encountered the most often; sometimes, celadonite is developed to an equal extent or is even predominant. In the basalts, celadonite commonly forms rims in the gas vesicles. In the outcrop, the presence of celadonite is recognized by the blue-green color of clayey material. Thanks to its characteristic color, the distribution of this mineral in rocks can be established by visual observations.

In Ejafjordur, northern Iceland, celadonite mineralization was revealed within the part of plateaubasalts in which secondary minerals were formed at temperatures below 100°C. This is the mesolite–scolecite-type zeolite zone (Kristmannsdottir, 1982; Kristmannsdottir and Tomasson, 1978). In this temperature zone, clay minerals are always formed first.

Conditions of the formation of the clay minerals from low-temperature solutions, as well as the causes of formation of various structural types of clay mineral aggregates (rims, fissure filling, sedimentation levels similar to parallel bands in onyxes, diverse offshoots on the vesicle walls; tubular and segmented formations, globules, etc.), remain unknown. To elucidate this problem, an investigation of the clay mineral compositions, as well as a study of the phyllosilicate aggregates of the smectite–celadonite group, were undertaken using a scanning electron microscope (SEM).

GEOLOGIC SETTING OF THE OBJECTS INVESTIGATED

Specimens were picked up in Ejafjordur, northern Iceland, from natural sections of the Miocene–Pliocene

plateaubasalts, within a height range from the sea level up to 200–300 m. Judging from the character of the interrelation with host rocks (horizontal banding in monoclinical sequence and the confinement of the maximum clay mineral accumulations to fracture zones, i.e., fracture–dike swarms), one can confidently suggest the superimposed genesis of the secondary mineral complex, including phyllosilicates.

Formation of the celadonite mineralization is paragenetically related to siliceous mineralization and is chiefly confined to the fracture–dike swarms. It was previously established that secondary mineral formation within this zone might be related to the inflow of ground waters which, on their way, washed silicic subvolcanic intrusions of central volcanoes (Geptner and Petrova, 1996).

Beyond the fracture–dike swarm, phyllosilicates are primarily represented by smectites; celadonite is lacking even in the sites where the basalt sequence contains interlayers and lenses of silicic ashes. This fact also can evidence that, within the upper, low-temperature zone, the secondary mineral is formed chiefly due to the introduction of elements by subsurface solutions, whereas the contribution of host rocks is minimal.

When discussing the biochemogenic manner of phyllosilicate formation, it is important to keep in mind that ground waters of Iceland are characterized by low total mineral content (Kononov, 1983). Therefore, it is reasonable to assume that one of the most important factors of precipitation of elements from the weakly mineralized solutions could be microbiological activity which, at the microlevel, facilitated the formation of chemical barriers and provided conditions favorable for generating the minerals under consideration.

CLAY MINERALS FROM THE ZEOLITE ZONE OF THE HYDROTHERMALLY ALTERED BASALTS

Phyllosilicates from low-temperature zones of the alteration of basalts have been examined in a large number of works, which are not required to be quoted here. The composition of phyllosilicates and their distribution in the basalts of Iceland are considered in (Kristmannsdottir, 1975, 1978, 1982; Mehegan and Robinson, 1982; and others). Based on the study of published data and our own data, it should be primarily noted that clay minerals, as well as other secondary formations are unevenly distributed within basalts of this hydrothermally altered zone. The intensity of secondary mineralization development is chiefly dependent on the permeability and jointing of rocks. The secondary mineralization strata transect the monoclinical plateaubasalt sequences. One can distinguish strata (occasionally, alternating and recurrent in the section) with different composition of clay minerals.

Diocahedral smectites are the most abundant within the basalt alteration zone under consideration. Triocahedral smectites are more rarely encountered, commonly being present in the mixture with diocahedral ones. Within the strata containing large amounts of plant organic matter (coals and lignites), smectites associate with halloysite and kaolinite. The appearance of celadonite, which is also commonly encountered in the plateaubasalts in assemblage with smectites, is very characteristic. Thanks to its specific blue-green color, the presence of celadonite can be established in an outcrop by visual observation; in microscopic investigations, this mineral can also be distinguished from other phyllosilicates, mainly smectites. Based on this, it has been established that the formation sequence of smectites and celadonites can differ in various sampling points even within a certain region.

All above-noted clay minerals are distributed within the upper, low-temperature part of the altered basalts. Since the variations in composition of the hosting basalts in the territory studied are insignificant, the composition of the waters from which the clay minerals were formed should greatly differ in each case. This suggests that the salt composition of the solution, which washed the upper section of the plateaubasalts, was formed primarily at deep levels of the section and at higher temperatures (for instance, near or within the bodies of central volcanoes). The elements were transported from these zones by water flows heated and were gradually consumed for the formation of various minerals (depending on temperature, peculiarities of mineral compositions, and crystallization conditions); simultaneously, the salt composition of the solution was changed and depleted. This mechanism of the salt composition transformation, which is caused by selective separation of elements in the course of mineral formation, manifested itself particularly prominently during the long-range migration of ground.

STRUCTURAL FEATURES OF THE CLAY MINERAL AGGREGATES

Clay aggregates of various types were optically analyzed in thin sections and in natural chips under a SEM.

Optically Distinguishable Structures

Among diverse aggregates of clay minerals, which have been observed within vesicles and microfissures in the basalts, the following frequently encountered formations can be noted.

(1) Rims covering the walls of gas vesicles or of cavities of other origin, as well as the walls of fissures. Within different cavities, the rims vary in thickness from a few fractions of a millimeter to 1.0–1.5 mm. The rims accurately copy all irregularities of the underlying substratum. In some cases, a layered structure of the rims is clearly seen, which is determined either by the difference in crystal dimensions or layer colors (for instance, grass-green, blue-green, yellow-green, and so on) (Fig. 1).

(2) So-called "sedimentation levels." In their structure, these formations resemble horizontally layered sediments that are accumulated in calm waters. In the case of clay mineral formation within vesicles and larger cavities, the sedimentation levels are usually changed upward by the rims, extending over the walls of these spaces (Fig. 2).

(3) "Threads" which branch and sometimes form felted clusters (Fig. 3a).

(4) Worm-shaped offshoots on surfaces of the rims or the sedimentation level formations (Fig. 3b).

(5) Globules of various dimensions and globule intergrowth clusters, sometimes similar in shape to a bunch of grapes (Fig. 3c).

(6) Intricate reniform aggregates consisting of individual spherical and oval bodies (Fig. 3d).

The structural types of clay mineral aggregates considered are encountered both singly and in diverse combinations.

Structural Features Revealed by the SEM Investigation

During the SEM investigation of some of the above-noted optically distinguished structural types of clay minerals, a number of nanostructural peculiarities have been revealed, which evidence their complicated formation. Only two types of structures will be considered below—namely, worm-shaped structures and globules—because it is during their study that structural peculiarities have most clearly manifested themselves, which can be most reasonably explained by the biogeochemical activity of microorganisms.

The worm-shaped formations vary in size from a few fractions of a millimeter to 0.5 cm or occasionally more. They are intricately curved and sometimes ramified.

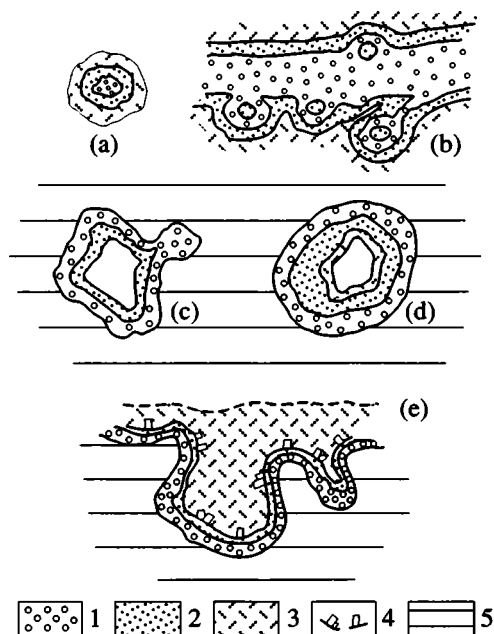


Fig. 1. Structural peculiarities of clay mineral aggregates in basalts (optical microscope, magn. 50–200). Zonality of clay formations, marked by different colors. (a, b) Biomorphic structures; (c, d) phyllosilicates within gas vesicles in basalts; (e) large cavity in basalt (appearance of zeolites marks a pause in phyllosilicate formation). (1) Dark-green, (2) blue-green, (3) pale green, (4) zeolites, and (5) basalt.

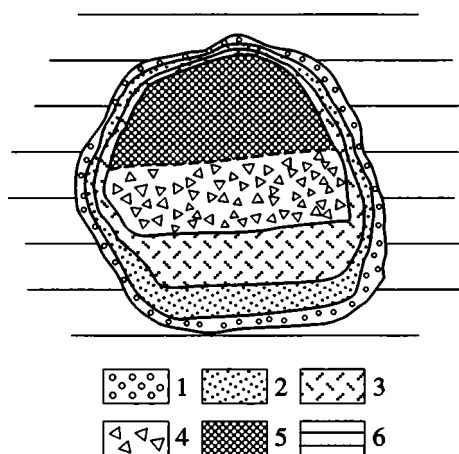


Fig. 2. An example of sedimentation of fine-dispersed phyllosilicate particles and formation of sedimentation-type structure. (1–3) Differently colored phyllosilicates (symbols as in Fig. 1), (4) zeolites, (5) calcite, and (6) basalt.

Even at a low magnification, a concentric-zonal structure with a clearly defined central core is evident in cross sections of the worm-shaped aggregates. Sometimes, one or several round longitudinal channels are seen at the center rather than the core. Three or four zones of phyllosilicates are clearly recognized, which are distinguished by the nanostructure due to different forms and dimensions of the constituting crystals. Bod-

ies of the individual zones are commonly located close to each other, but in some vermicular aggregates, it can be seen that such zones are separated by microvoids (Fig. 4).

The oval and round openings on the surface of the worm-shaped formations are unevenly distributed. It is noteworthy that the smooth outlines of these openings are formed (as though enveloped) by acicular, elongated, curved crystals (Figs. 3 and 5). These openings vary from 1 to 20 μm in size.

The dense core in the central part of such an aggregate has a cellular surface with various dimensions of the cells (3–5 μm across). Within each cell, a globule occurs with its surface covered by thin “petals” of phyllosilicates. These globules resemble siliceous lepispheres. The surface of the central core has the same structure, whereas the interior of the core is composed of a dense homogeneous material. Sometimes the external zone of the vermicular aggregates is composed of elongated, acicular or lath-shaped, crystals (obviously, of celadonite) constituting a crustification rim. Within a free space between the vermicular formations, the similar but rare, large and strongly elongated lath-shaped crystals occur.

The biogenic nature of the object is confirmed by the sectional character of the central core structure. As seen in Fig. 6a, such a structure is well developed even when the core is composed of quite large scaly crystals of phyllosilicates. Elongated sections of the core are separated by transversely oriented aggregates of “leaflets” of the same type and size. On the surface of the inner zone of the vermicular aggregate, the sectional structure appears clearly as well, but it is complicated by a large number of spherical bodies varying from 2–5 to 10 μm in size.

At the present time, the following three types of spherical bodies can be distinguished according to the shape of the constituting crystals:

(1) Spherical bodies confined to the core surface. As it has been already noted above, these balls universally occur within hollows and are covered with scaly, sometimes curved crystals similar to those covering the surface of the core itself.

(2) Spherical bodies within the free space between the vermicular structures, which are composed of large, lath-shaped and rod-like crystals. They are in contact with the few elongated crystals of the external crustification rim of the vermicular aggregates. There is much free, unoccupied space around the globules.

(3) Globules covered by radially oriented acicular crystals (Figs. 6b–6d).

Examining the separate vermicular aggregates and their composite intergrowths, it is very important to note the presence of numerous round, oval, and irregular openings on their surfaces. A common morphological feature of such openings is smooth outlines formed by individual acicular and lath-shaped crystals, which sometimes coalesce into a continuous thin film. It is

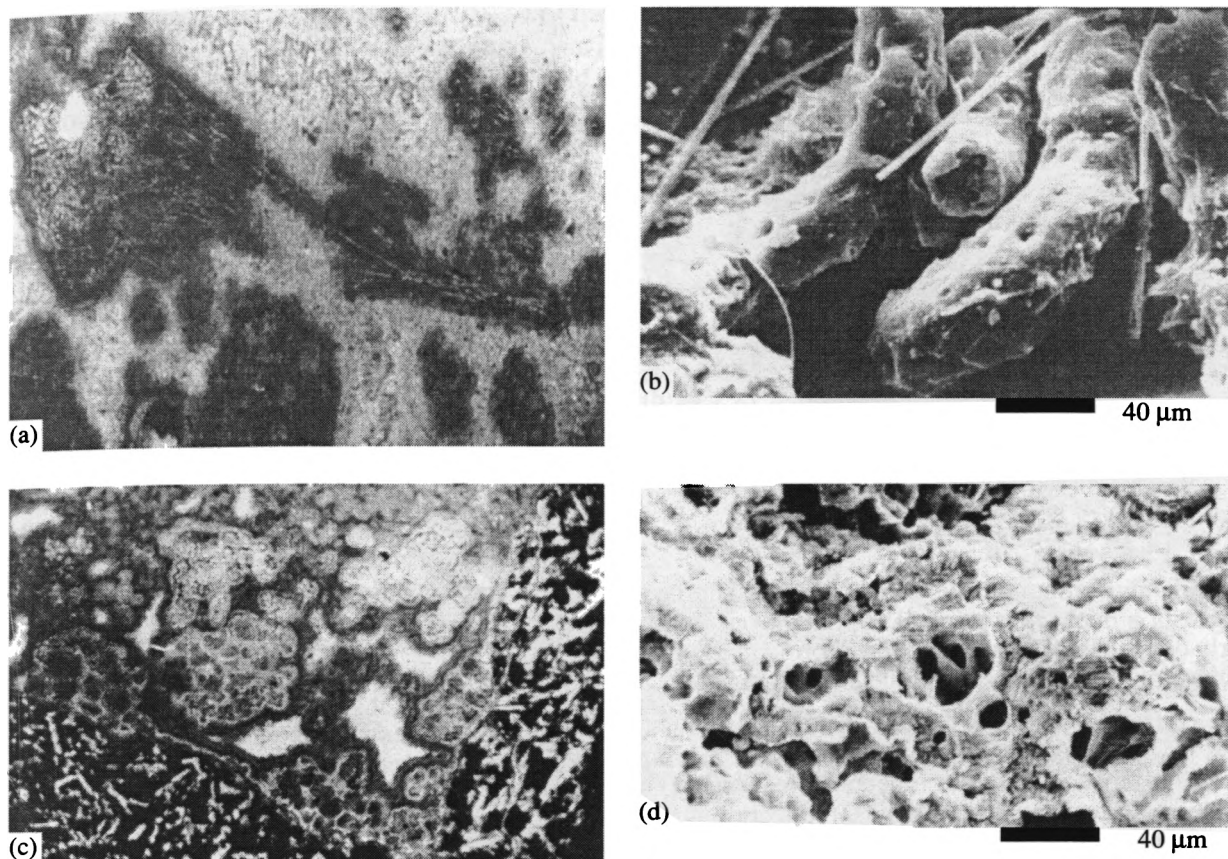


Fig. 3. Biomorph structures composed of phyllosilicates. (a) Branching filiform structures (optical microscope, magn. 150); (b) vermicular offshoots on concentric films covering the walls of cavities in basalts: on the surface contains numerous openings; the cross section reveals a rounded channel in the center (SEM image); (c) globules and their irregular intergrowths with zonal or lumpy internal structure (optical microscope, magn. 150); (d) intricate combination of above-specified structures forming rounded and oval (sometimes, resembling reniform) aggregates with numerous intersecting channels and cavities (SEM image).

conceivable that a intricately branching body with smooth outlines previously existing was formerly covered by this film. Tiny openings with smooth outlines are encountered even in single petal-shaped crystals.

The above-noted peculiar features of the examined structural elements evidence that the phyllosilicates were formed around a certain material substratum involved in their formation, which was subsequently dissolved and then disappeared. It seems to be most likely that such substratum might be represented by living organic matter, and that the nanostructures found were possibly of bacterial genesis (bacterial mats).

CHEMICAL AND MINERAL COMPOSITION OF THE BIOMORPHIC AGGREGATES OF PHYLLOSILICATES

Analysis of the chemical composition of a vermicular aggregate in its cross section, performed using a SEM and a LINK-860 analyzer, has shown a predominance of Si, Fe, and K over other elements and a rather monotonous distribution of Si, K, Fe, Mg, and Al throughout the various structural zones (Fig. 7).

At the same time, a microprobe analysis of different pieces of the vermicular aggregate, picked up from a specimen, has revealed noticeable variations in the chemical composition (table).

Tentative calculation of structural formulas¹ (numbers correspond analysis numbers in table).

1. $K_{0.73}Na_{0.01}(Si_{3.94}Al_{0.06})_{4.00}(Al_{0.15}Fe_{1.27}^{3+}Mg_{0.52})_{1.94}$
(celadonite)
2. $K_{0.36}Na_{0.08}Ca_{0.09}(Si_{3.70}Al_{0.30})_{4.00}(Al_{0.05}Fe_{1.50}^{3+}Mg_{0.51})_{2.06}$
(nontronite)
3. $K_{0.64}Na_{0.01}(Si_{3.66}Al_{0.29}Fe_{0.05}^{3+})_{4.00}(Fe_{1.63}^{3+}Mg_{0.39})_{2.02}$
(nontronite, probably mixed-layer species with glauconite)
4. Si-Ca-Fe-Al-K hydrogel.

A diffractometric study of vermicular clay sample picked up under a microscope evidences that zeolites of

¹ The structural formulas were calculated on the basis of $O_{10}(OH)_2$ anion framework for 1/2 unit cell.

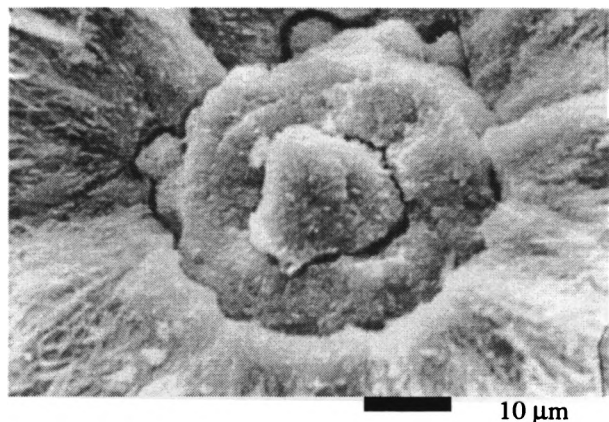


Fig. 4. Zonal structure of the cross section of the vermicular aggregates (SEM image).

the heulandite–clinoptilolite series are present here along with a micaceous mineral. Optical investigation clearly demonstrates that the zeolites formed later than the clay minerals. They seal all the clay aggregates.

The diffraction pattern of an air-dry oriented preparation of the micaceous mineral at demonstrates an almost integer series of basal reflections with $d(001) = 9.98 \text{ \AA}$; in this case, the $I(001)/I(002)$ reflection intensity ratio suggests a substantially high content of Fe in the mineral. Zeolite is identified by the 020 reflection with d equal to $8.9 \text{ \AA}$.

To study the composition in greater detail, samples of clay minerals of four types, according to their shape and color, were extracted from this same specimen in dry state under a microscope. These types were:

(I) “worms” with the light-green surface; (II) fragments and central parts of the “worms,” consisting mainly of blue-green clay material; (III) light-brown clay material occurring at the surface of some “worms” and between them; (IV) tiny dark-green nodules resembling globular glauconite in shape.

Using X-ray diffractometry, the affinity of the I and II types to micaceous minerals has been established. Their diffraction patterns are analogous, each contains two basal reflections, with $d(001) = 9.85 \text{ \AA}$ and $d(003) = 3.31 \text{ \AA}$, for the air-dry samples, and $d(001) = 9.8 \text{ \AA}$ and $d(003) = 3.32 \text{ \AA}$, for the samples saturated with ethylene glycol. The effect of insignificant 001 reflection shift toward larger angles on saturation of the sample with ethylene glycol indicates the presence of single swelling interlayers in the mineral structure; the relatively low $d(001)$ value of the reflections of the air-dry samples evidences that Na cations, along with K ones, are present within interlayer spacings in the mineral structure.

Because only a small amount of the material was available, the diffraction images of the studied samples were scanty and it was impossible to carry out their more detailed identification using the X-ray diffraction technique. This refers to types III and IV as well, which are characterized by one weak low-angle reflection each. Sample III is assigned to smectite; its $d(001) = 12.6 \text{ \AA}$, can serve as an indicator of occupancy of interlayer spacings in the mineral structure primarily by Na cations. Sample IV is represented by mixed-layer illite–smectite with $d(001)$ equal to $10.28 \text{ \AA}$ in air-dry state, and to $9.8 \text{ \AA}$, after its saturation with ethylene glycol. The structure of this mineral contains approximately 25% of swelling interlayers.

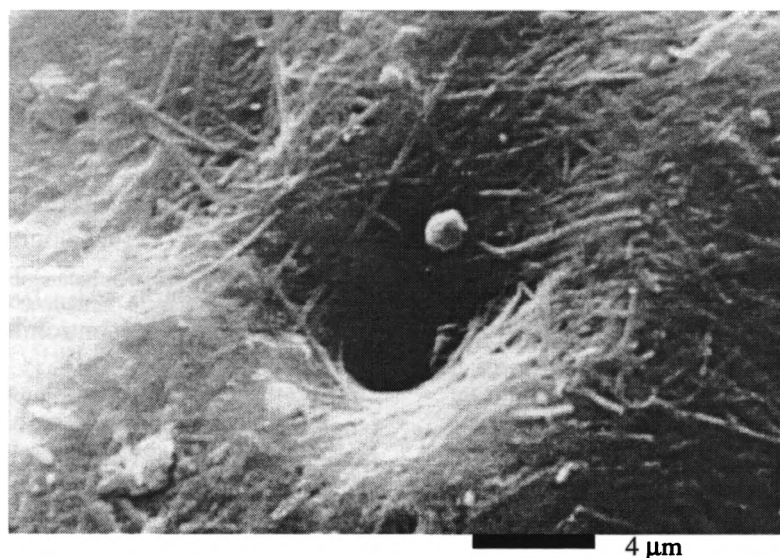


Fig. 5. Character of occurrence of acicular celadonite(?) crystals along the edges of openings on a vermicular aggregate surface (SEM image).

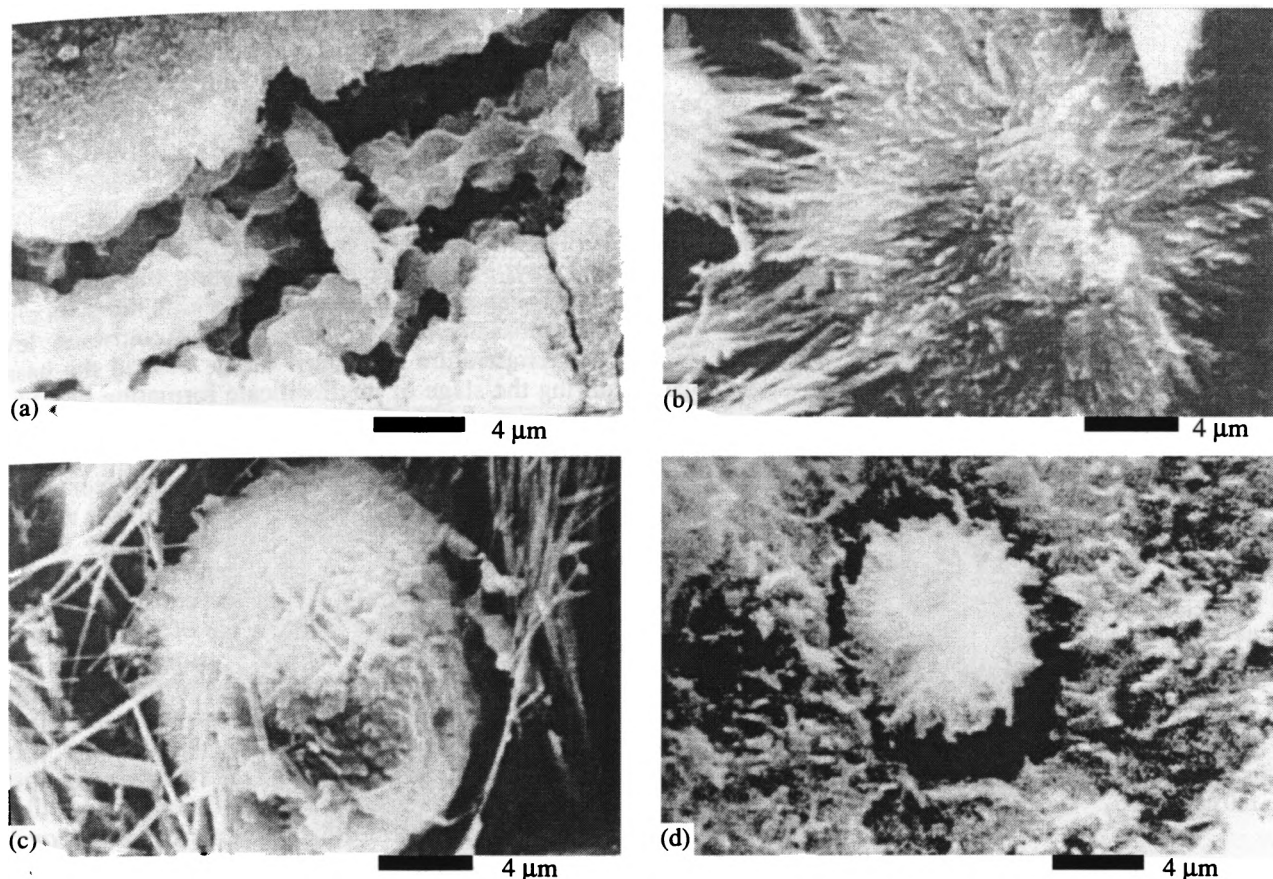


Fig. 6. Nanostructures of some of the biomorphic formations observed. (a) Sectional structure of the central core of a vermicular aggregate; (b, c, and d) types of spherical structures (SEM images).

Examination of the data obtained does not enable one to determine with sufficient certainty the mineral composition of the phyllosilicates constituting the vermicular aggregates. However, the tentative calculations of the structural formulas and the diffractometric data available allow one to suppose that the major role in the structure of the formations analyzed is played by nontronite with noticeable participation of micaceous minerals. It can be confidently suggested that a celadonite component is present in the composition of these minerals. Some sectors of the biomorphic aggregates may have been composed of the as yet uncrystallized Si-Ca-Fe-Al-K hydrogel.

Interesting results have been obtained during investigation of the character of major component distribution in the rims of clay material that fills, in association with zeolites, small vesicles in a basaltic lava flow. Potassium has been noted to form isolated, irregular patches in the field of Fe-phyllosilicates (Fig. 8). It is possible that the uneven distribution of K is caused by a change in geochemical conditions within microvolumes of the environment during the phyllosilicate origination. This phenomenon might be related to microbi-

ological activity and to the local formation of K-containing gel. It has been shown above that the studied biomorphic phyllosilicate aggregates contain a lot of K.

AGE AND THERMAL CONDITIONS OF FORMATION OF THE BIOMORPHIC AGGREGATES

The biomorphic structures under consideration were found in the monoclinial plateaubasalts which are transected by subhorizontal zones of secondary mineralization (Palmason *et al.*, 1979). This makes it possible to establish the lower age limit of the secondary mineralization, which appears to be significantly younger than all the plateaubasalts cropped in this area. The specimens for investigation were picked up from the base of the section which has the total thickness of more than 700 m. It is the mesolite-scolecite zone of zeolitization formed at a temperature of about 70–90°C (Kristmannsdottir and Tomasson, 1978). It is also necessary to take into account that a significant part of the plateaubasalts has been removed by exaration. Therefore, it is reasonable to suppose that the secondary min-

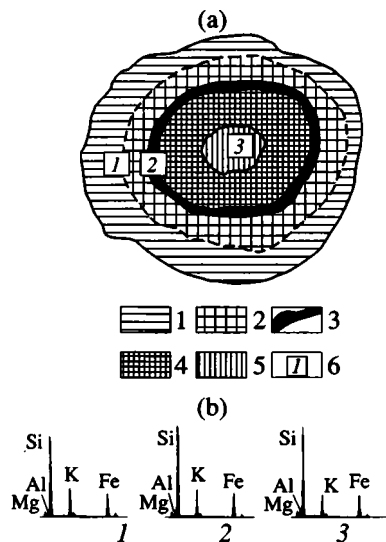


Fig. 7. Major element distribution in different zones of a vermicular aggregate (cross section). (a) Petrographic features: (1) thin, acicular crystals (beige-colored zone); (2) the same (light-green zone); (3) zone of homogeneous structure (dark-green, nearly black zone); (4) closely packed isometric crystals (blue-green zone); (5) zone of homogeneous structure (grass-green); (6) spots analyzed for the elementary composition (see Fig. 7b). (b) Element distribution in the spots specified in Fig. 7a. The biomorphic structure is 100 μm across.

erals under consideration were formed at a depth of several hundreds of meters below the ground surface. As noted above, phyllosilicates were formed first in the association of secondary minerals. They are commonly sealed by zeolites, siliceous minerals (opal, chalcedony, quartz), and, more rare, calcite, or by the association of all these minerals. In the specimen of vermicular phyllosilicates, other secondary minerals are represented only by zeolites, among which mordenite and heulandite have been detected. Examination of thin sections containing the siliceous minerals has demonstrated that quartz and chalcedony, which often seal the biomorphic formations of phyllosilicates, possess numerous

structures, which are revealed in reflected light, that allow one to believe that the siliceous material originally precipitated as a gel. This is considered more fully in the special work (Geptner and Petrova, 1996).

DISCUSSION

The data available can be summarized in the following way. Phyllosilicates constituting the diverse biomorphic aggregates were formed within the monoclinical plateaubasalts located below the groundwater level. The temperature of waters which washed the basalts during the stage of phyllosilicate formation was likely no more than 100°C. The confinement of the celadonite (glauconite or, generally, micaceous) mineralization to a fracture-dike swarm spatially related to a central volcano make it possible to determine the upper age limit of the secondary mineral formation. This volcanic structure includes felsic subvolcanic intrusions, which crosscut the plateaubasalts under consideration. The felsic intrusions could be a source of K supply to the low-K basalt sequence. It can be supposed that other elements required for the existence of the microorganisms were also introduced with ground waters heated within a high-temperature halo of the central volcano. It is difficult to suggest now the kind of microorganisms that might exist under such conditions. Most likely, they were chemolithotrophic bacteria which *can use inorganic compounds or ions (ammonium, nitrite, sulfide, thiosulfate, sulfate, and bivalent iron ions), as well as elementary sulfur, molecular hydrogen, and CO, as donors of hydrogen or electrons; i.e., they are able to obtain, as a result of oxidation of these compounds, the reducing equivalents and energy for synthesis processes* (Schlegel, 1985, p. 348). In other words, an ecosystem existed in the subsurface heated waters in which the biomass production was not based on photosynthesis, but on chemolithoautotrophy.

It has been long known that bacteria are involved in the origination of a number of mineral formations of sedimentary deposits. Recently, the most important role of bacteria in the formation of nontronites within

Results of microanalysis of the vermicular aggregates of phyllosilicates

Oxides	1	2	3	4	5	6	7	8
SiO ₂	49.68	50.48	40.99	24.93	50.52	53.11	43.12	37.57
Al ₂ O ₃	2.31	4.10	2.78	10.89	3.64	2.99	3.13	3.16
Fe ₂ O ₃	21.32	27.22	25.13	3.75	25.43	22.04	221.73	21.66
CaO	0.00	1.18	0.01	5.20	1.13	0.00	0.00	0.00
MgO	4.34	4.65	2.87	0.41	4.66	4.42	3.82	3.87
K ₂ O	7.18	3.81	5.64	1.57	4.30	7.70	7.53	7.50
Na ₂ O	0.07	0.56	0.09	0.04	0.40	0.90	0.00	0.00
Total	84.90	92.02	77.51	46.78	90.26	90.34	79.33	73.76

Note: (1–8) are the numbers of specimens.

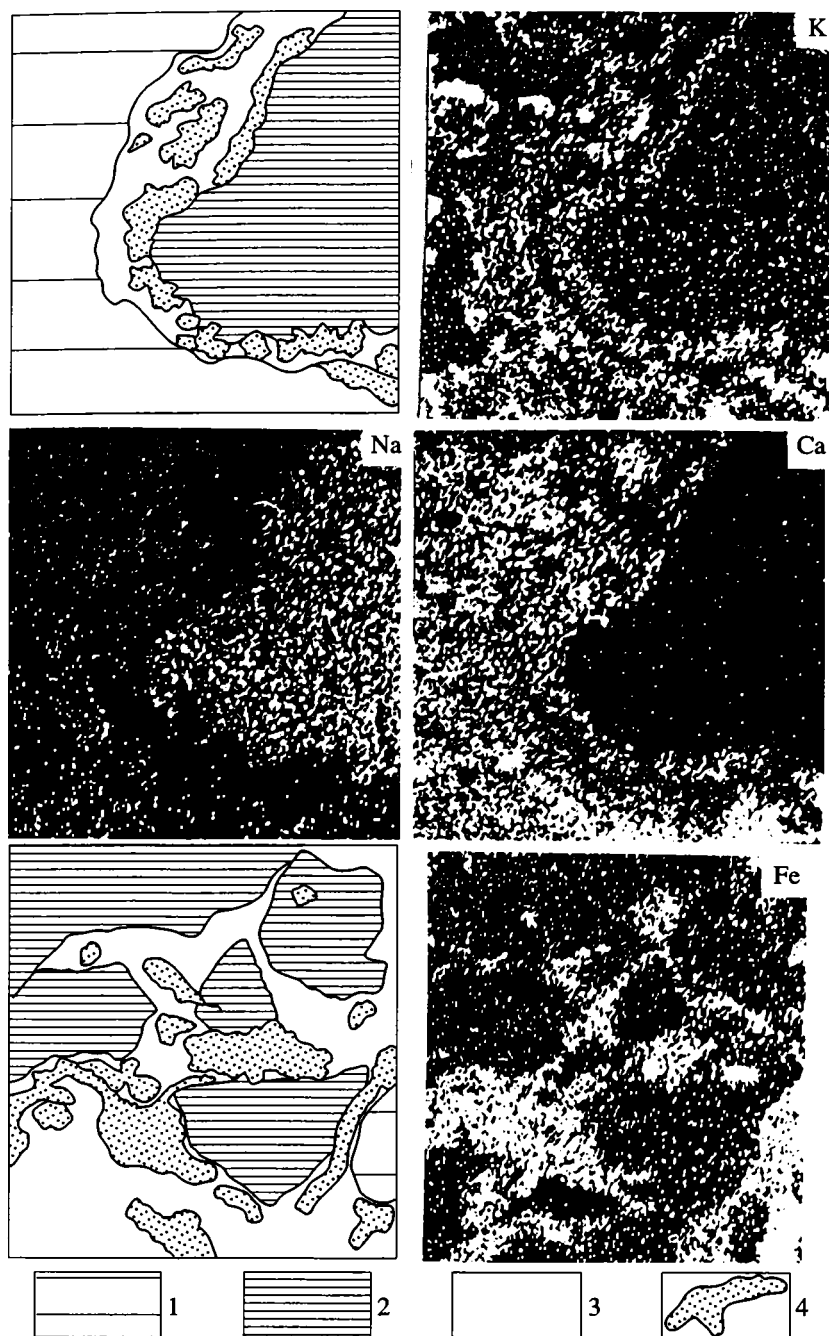


Fig. 8. Potassium distribution in clay minerals (a) covering the surface or (b) filling the cavities in basalts. Na- and Ca-Na-zeolites fill a space left open after clay mineral formation. (1) Basalt, (2) zeolites, (3) clay minerals, and (4) areas of K concentration in the clay minerals.

the zone of activity of so-called white smokers has been established with certainty (Kohler *et al.*, 1994). This, as well as the above-considered data, allows one to believe, that the effect of bacterial activity on the phyllosilicate formation within the basalt sequence subsided to a significant depth is very probable.

The structural peculiarities of the biomorphic aggregates, as well as the character of their interrelation with the host rocks and with the paragenetic complex of sec-

ondary minerals, make it possible to consider these formations as a result of bacterial action on the mineral-forming environment, causing the appearance, within a microvolume, of conditions favorable for concentration of the elements required subsequently for origination of the smectite–celadonite mineral complex. The substantial role of microorganisms in the phyllosilicate formation follows from the fact that weakly mineralized low-temperature waters hosted by fresh or weakly altered

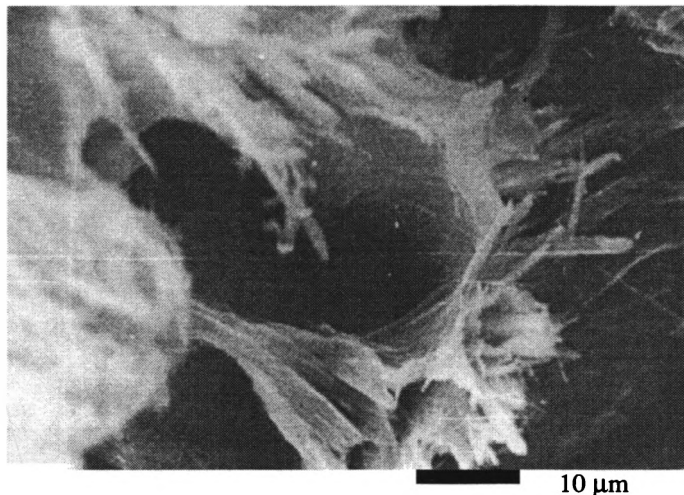


Fig. 9. Openings and channels in a smectite-celadonite rim on the cavity wall in basalt: relics of once existing organic matter that filled these spaces (SEM image).

rocks are not the environment in which these minerals can be formed by a purely chemical way. In contrast, it is easy to imagine the formation of Si-Al-Fe-K gel—a precursor of smectite, smectite-celadonite, or even pure celadonite—as a result of microbiological activity (oxidation of sulfur, hydrogen sulfide, bivalent iron, and molecular hydrogen, accompanied by reduction of sulfate to sulfide, or CO₂ to methane, and so on) even within a weakly mineralized environment.

Clear markers of biomorphic mineralization are preserved only in the case when a fossilized organic body is much larger than crystal individuals formed as a result of the gel crystallization. Therefore, it is unlikely that fine details of the original shape of biochemogenic gel matter have been preserved in the cases when we encounter either distinctly coarse-crystalline formations, such as the crustification rims on the cavity walls, or evidences of secondary recrystallization of clay minerals.

Apart from direct indicators of the similarity between the phyllosilicate aggregates and biogenic objects, an important evidence of the participation of living substance in the synthesis of this group of minerals is provided by diverse microscopic openings and channels (which, according to data we have in our disposal, vary from 0.5 to 30 μm in size), penetrating all the mineral aggregates and individual crystals. The organic matter rapidly disappears, but the remaining cavities with rounded outlines—even where the phyllosilicates are represented by elongated, smoothly curved acicular or lath-shaped crystals—may be considered, with a great share of certainty, to be relics which have retained outlines of the organic substance once existing (Figs. 4 and 9).

Formation of the rims on the cavity walls and the accumulation of so-called sedimentation levels can be assigned to the biochemogenic type with much less certainty. Nev-

ertheless, the microorganism participation might be of crucial importance in formation of the phyllosilicate aggregates of these structural types. In this case, the principal role of bacteria was in formation of tiny particles of Si-Al-Fe gel, which were more or less uniformly distributed in the solution. If the amount of the gel particles was small, they were electrostatically attracted to and precipitated on the cavity walls rather evenly, forming rims which often have a zonal structure. In contrast, if the formation of the particles was accelerated, they, sticking together and transforming into larger ones, gradually sank, under gravity, to the cavity bottom and formed, by such a way, the sedimentation levels.

CONCLUSION

The confinement of the smectite-celadonite mineralization to a fracture-dike swarm, transecting the plategbasalt monocline, suggests the superimposed character of the secondary mineralization and its formation in the course of washing of the basalts by ground waters.

Within the part of the section studied, judging from the available data, phyllosilicates formed at low temperatures from weakly mineralized solutions, of which the interaction with the host rocks was very insignificant.

The investigation of microscopic and nanostructural peculiarities of the layer minerals has revealed a number of structures bearing clear indications of living substance participating in synthesis of Si-Al-Fe-K gel, a precursor of these minerals. They are diverse vermicular, curved, and ramified aggregates with the concentric-zonal structure as well as spherical formations and their composite intergrowths constituting solid masses. Apart from the definitely biomorphic formations, the involvement of living substance into the mineral formation is evidenced by round and oval openings and chan-

nels encountered in solid masses of clay material. The characteristically smooth outlines of the openings and channels, as well as coating of elongated crystals on their walls, allow one to consider, with a great deal of probability, these formations as relic ones, which had witnessed once existing organic matter.

ACKNOWLEDGMENTS

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REFERENCES

- Geptner, A.R. and Petrova, V.V., Siliceous Minerals in Basalts of Iceland: The Composition and Conditions of Formation, *Litol. Polezn. Iskop.*, 1996, no. 1, pp. 32–43.
- Kohler, B., Singer, A., and Stoffers, P., Biogenic Nontronite from Marine White Smoker Chimneys, *Clay Clay Minerals*, 1994, vol. 42, pp. 689–701.
- Kononov, V.I., The Geochemistry of Thermal Waters in Recent Volcanism Areas: Rift Zones and Island Arcs, *Tr. GIN*, 1983, issue 379.
- Kristmannsdottir, H., Alteration in the IRDR Drill Hole Compared with Other Drill Holes in Iceland, *J. Geophys. Res.*, 1982, vol. 87, no. 8, pp. 6525–6531.
- Kristmannsdottir, H. and Tomasson, J., Zeolite Zones in Geothermal Areas in Iceland, *Natural Zeolites, Occurrence, Properties, Use*, Sand, L.B. and Mumpton, F.A., Eds., New York: Pergamon, 1978, pp. 277–284.
- Kristmannsdottir, H., Hydrothermal Formation of Clay Minerals in Icelandic Geothermal Fields, *Third Meeting of the European Clay Groups, Oslo: Volume of Summaries*, Oxford: Pergamon, 1977, pp. 87–90.
- Kristmannsdottir, H., Types of Clay Minerals in Hydrothermally Altered Basaltic Rocks, Reykjanes, Iceland, *Jökull*, 1976, vol. 26, pp. 30–39.
- Kristmannsdottir, H., Clay Minerals Formed by Hydrothermal Alteration of Basaltic Rocks in Icelandic Geothermal Fields, *Geol. Foeren. Stockholm Foerh.*, 1975, vol. 97, pp. 289–292.
- Mehegan, J.M. and Robinson, R.T., Secondary Mineralization and Hydrothermal Alteration in the Reydarfjörður Drill Core, Eastern Iceland, *J. Geophys. Res.*, 1982, vol. 87, no. B8, pp. 6511–6524.
- Palmason, G., Arnorsson, S., Fridleifsson, I.B., Kristmannsdottir, H., Saemundsson, K., Stefansson, V., Steingrímsson, J.B., Tomasson, J., and Kristjansson, L., The Iceland Crust: Evidence from Drillhole Data on Structure and Processes, *Deep Drilling Results in the Atlantic Ocean: Ocean Crust, Maurice Ewing Ser.*, Talwani, M., Harrison, C.G., and Hayes, D.E., Eds., Washington, 1979, no. 2, pp. 43–65.
- Schlegel, H.G., *Allgemeine Mikrobiologie*, Stuttgart: Georg Thieme, 1985.

Middle Jurassic–Lower Cretaceous Rock Assemblages in the Accretion Structure of the Taigonos Peninsula

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Abstract—Structural and compositional rock assemblages of the Penzhina–Anadyr fold system in the Povorotnyi Cape region of the eastern Taigonos Peninsula (the Penzhina Gulf) have been considered. Sedimentation processes and settings have been reconstructed based on lithological, mineralogical, and petrochemical features of sedimentary rock complexes. It has been established that sedimentation in the Middle Jurassic–Early Cretaceous was influenced by the active continental margin and simatic island arc. Possible paleolateral series of sedimentation zones have been considered.

The territory of the Taigonos Peninsula that is located in the western Penzhina Gulf of the Sea of Okhotsk (Fig. 1) is one of the key regions for understanding the Mesozoic history of the East Asian continental margin. Polygenetic structural and compositional rock assemblages of the peninsula are confined to the junction of the Koni–Taigonos and Penzhina–Anadyr fold systems (Nekrasov, 1976; Zaborovskaya and Nekrasov, 1977; Sokolov, 1992). The Koni–Taigonos system incorporate the Northern Taigonos (rear) and Southern Taigonos (axial) zones of the Taigonos segment of the Jurassic–Early Cretaceous Uda–Murgal volcanic arc (Zaborovskaya and Nekrasov, 1977).

It is believed that the Uda–Murgal volcanic zone initiated on the continental crust. Related effusive rocks are close in chemical composition to the Andean-type active margin volcanics, whereas terrigenous rocks contain erosion products of metamorphic rocks and granitoids. The Penzhina–Anadyr system incorporates island-arc and oceanic rock assemblages that compose complicated accretion structure (Sokolov, 1992). The suture structure in the fold system junction is represented by the belt of Early Cretaceous gabbroid and granitoid rocks.

Though the tectonic structure of the above-mentioned region was considered in many works (Chekhov and Palandzhan, 1994; Gel'man and Nekrasov, 1968; Livshits, 1972; Nekrasov, 1976; Nekrasov *et al.*, 1970; Zaborovskaya, 1978; Zaborovskaya and Nekrasov, 1977; Zagruzina and Smirnov, 1973; Zhulanova, 1974, 1975a, 1975b, 1990; and others), many aspects of stratigraphy and evolution of the region remain unclear. The geodynamic history of the region was never considered on the basis of sedimentary rock assemblages

that represent most important indicators of the paleotectonic regime in sedimentary basins.

This paper deals with the structural and compositional features of rock assemblages in the Povorotnyi Cape region of the Penzhina–Anadyr fold system (Fig. 1) and is aimed at the correlation of sedimentary rock assemblages to reconstruct their formation settings based on lithological mineralogical, and petrochemical signatures.

METHODS OF STUDY

The study of sedimentary rocks included the analysis of genetic indicators based on mineralogical, petrographical, and chemical features. To evaluate the content of rock-forming constituents and interpret the data of the chemical analyses, medium- and fine-grained sandstones (0.25–0.5 to 0.1–0.25 mm fractions) were used.

When evaluating the geodynamic background of deposition, rock varieties enriched in tuffaceous material and tuffs as well as rocks with an elevated calcium carbonate content were excluded from the consideration. The quantitative mineralogical analysis was made by A.V. Andreev; the silicate and quantitative spectral analyses were performed by N.L. Kalashnikova and I.Yu. Lubchenko, respectively, in the Analytical Center of the GIN.

THE SECTION STRUCTURE

Structural and compositional rock complexes of the Penzhina–Anadyr fold system studied in the coastal cliffs of the Taigonos Peninsula from the Vitaetglya River mouth to the Povorotnyi Cape area form a complicated thrust and fold structure of the eastern vergence (Fig. 1). The section is comprised of ophiolites,

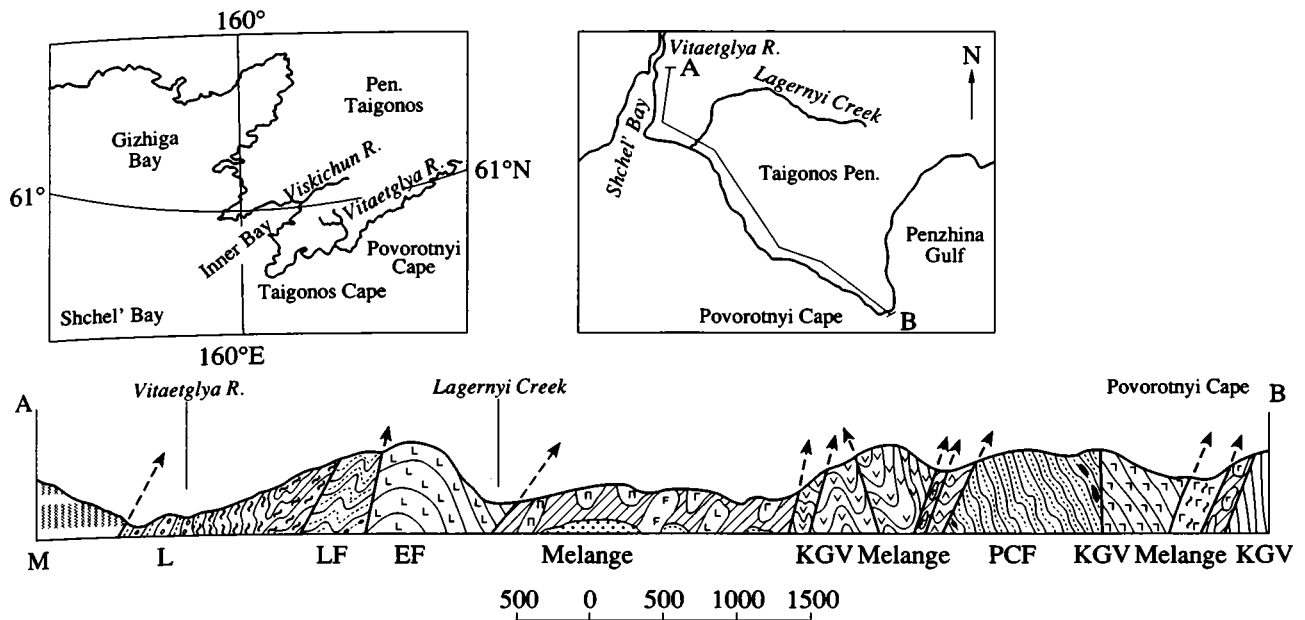


Fig. 1. Location of the studied area and geological cross section along the line A–B. Lithologic units: (M) Myalekasyn, (L) Lagernyi, (Ef) effusive, (KGV) Kingiveem, (LF) Lagernyi flysch, and (PCF) Povorotnyi Cape flysch.

volcanogenic–siliceous, and various terrigenous deposits of Middle Jurassic–Early Cretaceous age. Rocks of the Lagernyi and Myalekasyn units compose the northeastward overturned synform that is traced from the Taigonos Bay in the southwest to the lower and middle courses of the Vitaetglya River to coastal cliffs of the Penzhina Gulf in the northeast. Synform limbs are composed of slump deposits of the Lagernyi Unit. The synform core is filled with coarse-grained deposits of the Myalekasyn Unit. The study cross section demonstrates only a small part of the southern flank of synform.

The Myalekasyn unit of Hauterivian–Barremian age (Nekrasov, 1976) was studied in the small block near the Vitaetglya River mouth (Fig. 1) and the right side of its middle course. In the first locality, coarse-clastic volcanomictic rocks have a tectonic contact with intensely deformed and milonitized volcanogenic–sedimentary deposits of the Lagernyi Unit. Two subunits are observed in the middle course of the Vitaetglya River: the lower subunit composed of gritstones and sandstones (less commonly of boulders, gritstones, and sandstones) and upper subunit consisting of sandstones, siltstones, and mudstones. The upper subunit contains members (1–5 m) of banded cherts, often dislocated into small open folds, siltstones with flattened pebbles of gray and black cherts, and recrystallized limestones. In this paper, we consider data on the lower subunit.

The Lagernyi unit was traced from its contact with Myalekasyn Unit along the left side of the Shchel' Bay in the vicinity of the Vitaetglya River mouth where it gives way to the relatively small block of flysch rocks

with an indistinct boudinage structure (Fig. 1). The Lagernyi deposits and flysch rocks were previously referred to the Kingiveem Unit that is distributed farther southeastward (Nekrasov, 1976). We first distinguish the Lagernyi deposits as a separate unit, because it differs both from the Kingiveem unit and the flysch block rocks, which we refer to the flysch unit. Based on the structural position and compositional similarity with the Myalekasyn rocks, the age of the Lagernyi Unit is considered to be post-Valanginian (Hauterivian–Barremian).

The effusive unit was traced from the block of the Lagernyi flysch to the Lagernyi Creek mouth where it has a tectonic contact with serpentinite melange (Fig. 1). The unit is composed of unaltered green, brown-red, crimson-colored, and yellow tuffs, tuffaceous breccia, hyaloclastites, and spheroidal lavas. Volcanics are intermediate to basic in composition and in geochemical parameters correspond to volcanics of ensimatic island arcs. Based on preliminary radiolarian datings by V.S. Vishnevskaya (Institute of the Lithosphere, RAS) and I.E. Pral'nikova (Geological Institute, RAS), the age of these rocks is determined as Triassic–Jurassic.

G.E. Bondarenko sampled rhythmically bedded members of the terrigenous flysch incorporated in effusive rocks of the considered unit. The petrographic composition of sandstones from these members is identical to that of sandstones from the Lagernyi flysch unit (Fig. 1). M.V. Aleksyutin (GIN RAS) collected buchias and inocerams from the tectonic wedge that is exposed along the western coast of the Shchel' Bay in the continuation of the effusive unit and referred to the Lager-

nyi flysch unit. According to V.P. Pokhialainen, North-western Complex Research Institute, Magadan, the fossils sampled are characteristic of the Upper Jurassic–Lower Cretaceous (Volgian–Valanginian) time. The unit, as an independent element of the section, is defined for the first time, although some researchers (Chekhov and Palandzhan, 1994) noted that the “island-arc” signature of its volcanics, the freshness of the effusive–pyroclastic material, and the subordinate role of siliceous rocks differ it from the Kingiveem rocks. Similar volcanics are known along the northwestern framing of the Penzhina–Anadyr system (for instance, in the middle and upper courses of the Vitaetglya River).

The serpentinite melange is exposed in coast cliffs southeastward of the Lagernyi Creek where it has a tectonic contact with the Kingiveem deposits (Fig. 1). Narrow serpentinite bands also cross the Kingiveem deposits southeastward of the main contact. The melange deposits near the Lagernyi Creek are composed of slightly serpentinitized massive to banded lherzolites and harzburgites, gabbro, as well as dunite, diabase, and spilite blocks along with garnet amphibolites and eclogites.

The Kingiveem unit represented by the alternation of oceanic tholeiitic basalts and cherty–jasper rocks is exposed southward from the melange zone up to the Povorotnyi Cape area. Spilites are weakly foliated and show low-temperature alterations. V.S. Vishnevskaya (Institute of Lithosphere) determined the Middle Jurassic–Early Cretaceous radiolarian assemblage from siliceous rocks distributed westward of the flysch zone in the Povorotnyi Cape area. On the whole, the age of the unit in different areas of the Taigonos Peninsula widely vary from the Late Triassic to Early Neocomian (Chekhov and Palandzhan, 1994; Nekrasov, 1976).

The flysch unit comprises terrigenous rocks outcropping in spatially isolated blocks and tectonic wedges. In this paper, sandstones from two blocks are considered in detail. The first block is located in the southern flank of the Lagernyi Unit area and the other one, in the Povorotnyi Cape area (Fig. 1). To make the description and presentation of petrochemical data more convenient, we define the Lagernyi Creek flysch and Povorotnyi Cape flysch. The age of these deposits differs in different blocks despite their similarity in composition. For instance, the age of the Lagernyi flysch is determined by radiolarians (M.V. Aleksyutina, GIN, analyst) to be the Latest Jurassic–Early Cretaceous (Volgian–Valanginian). Samples from the middle part of the flysch section of the Povorotnyi Cape area yielded radiolarians of Middle–Late Jurassic (Callovian) age (S.D. Sokolov, personal communication).

LITHOLOGY OF SEDIMENTARY ROCK COMPLEXES

The Myalekasyn unit. It is impossible to compile the combined section of this unit and to estimate its

thickness. The lack of good exposures makes diagnostics of rock genetic types difficult, however, in some washouts in the river bed, typical structures related to submarine gravity slumping were observed. These are graded sorting of the clastic material from boulder to gravel and sand, tiled jointing, as well as strata (chains in cross section) of oval-flattened (extended along the bedding) sandstone, siltstone, and mudstone pebbles. Large clasts and pebbles, which are commonly oriented parallel to the bedding are confined to the layer base. The pelite material content is insignificant; sometimes siltstone interlayers (1–5 cm) are present in the upper part of rhythmities. There are also rhythmities with peculiar Bouma structures. The thickness of separate beds is 1–1.5 m.

Structures and the coarse-clastic material reflect intense hydrodynamic regime of sedimentation. The absence of bedding in sandstones suggests quick material deposition by highly dynamic flows. The alternation of coarse and fine materials with gradual transitions within the single bed reflects their liquation that is also characteristic of highly dynamic flows. Normal graded sorting of the clastic material due to the relative displacements of clasts testifies to the lower concentration of suspensions and prolonged transportation of the clastic material as compared with flows, which form ungraded and inversely graded beds. This process is related to the discharge of high-density turbidity or grain flows (Walker, 1977).

The Lagernyi unit. This lithostratigraphic unit is represented by various sedimentary and volcanogenic rocks: basalts, limestones, siliciliths, jaspers, and tuffaceous flysch. Zones of intense milonitization are widely developed; their frequency and thickness increase northward in the direction of the Vitaetglya River mouth. Siliceous rocks are represented by bedded (3–5 cm) siliciliths that form members 2–5 m thick and by lenses of bright-red jaspers 5–10 cm thick. Marmorized limestones compose beaded beds (1–5 m) and isolated boudins in zones of intense milonitization. Aphyric foliated basalts dominate among volcanics that compose beds of 5–10 m in thickness.

The data available on the whole-rock composition of volcanics suggest that they belong to the calc-alkaline series and refer them to the ensimatic island arc rocks.

Sedimentary rocks are represented by intensely tectonized tuffaceous flysch. Relic genetic features suggest the formation of flysch rhythmities owing to discharge of submarine turbidity flows of the medium density. Relatively small (5–7 to 10–20 cm) thickness of beds, common presence of siltstone in rhythmite tops, predominance of fine- to medium-grained sandstones and the absence of slump structures suggest the relatively low hydrodynamics of submarine turbidity flows and the significant remoteness of the discharge zone from areas of the flow initiation. The abundance of the clayey–silty material and siliciliths with recrystallized radiolarians probably reflect the hemipelagic depositional setting.

The flysch unit. The Lagernyi flysch deposits have a tectonic contact with the Lagernyi Unit in the north and effusive unit in the south near the Shchel' Bay (Fig. 1). The Lagernyi flysch deposits show boudinage structures, however, they lack milonitization, a fact that distinguishes them from rocks of the adjacent Lagernyi Unit. The thickness of beds with boudinage structure varies from 5–7 to 10 cm.

The Povorotnyi Cape flysch deposits are exposed in the southeastern part of the peninsula. Approximately 1 km northwestward of the Povorotnyi Cape, the contact between flysch deposits and siliceous–volcanogenic rocks of the Kingiveem Unit can be observed. In general, the contact plane is parallel to the flysch occurrence (dip azimuth is 140°, dip angle, 82°–84°, reversed bedding).

Previously, it was shown with the Kuyul massif as an example that rocks of the Kingiveem Unit are present only in blocks of serpentinite melange and lack stratigraphic contacts with sedimentary formations of the region (Chekhov, 1982; *Kuyul'skii* ..., 1990). In the considered case, the basal part of the flysch section incorporates the stratum of slump deposits that contains large blocks of spheroidal lavas, lava breccias, and siliceous rocks of the Kingiveem Unit. In addition, a gradual increase in the sandstone maturity from green tuffaceous to terrigenous varieties was observed from the base upsection.

Field observation data allow us to suggest that the initial stratigraphic contact between these deposits was disturbed by later tectonic movements. In the northwest, Povorotnyi Cape flysch deposits are bounded by the narrow band of serpentinite melange.

The Povorotnyi Cape flysch deposits are well-stratified and slightly deformed. Seven members can be distinguished within this unit (Fig. 2):

Member 1 (0–50 m) is composed of nonrhythmic sandstones and siltstones. Fine-, medium- and coarse-grained (to gravel) sandstones as well as siltstones form beds 10–20 cm thick. A thin alternation of sandstones (5–10 cm) and siltstones (1–2 to 5 cm) is commonly observed. Sandstones are characterized by graded and less commonly, horizontally bedded structures. The base marks are not pronounced. Thin (10–15 cm) grit-stone strata are occasional.

Member 2 (50–180 m) consists of nine thick (5–8 m) layers of massive, mostly medium-grained sandstones divided by horizontally bedded mudstones, siltstones, and sandstones with a bed thickness of 10 cm. At the base of thick sandstone beds, strata of flattened mudstone and sandstone pebbles occur. Between beds 7 and 8 (from the base upsection) and at the base of bed 7, there are strata of slump deposits composed of oval, elongated silty mudstone fragments from a few centimeters to 1 m (less commonly 2 m) long occurring in the sandy-silty matrix. Erratic inclusions are absent; the composition of inclusions is similar to that of host rocks. Thin (0.5–1.3 m) discontinuous pockets (wedges) are filled

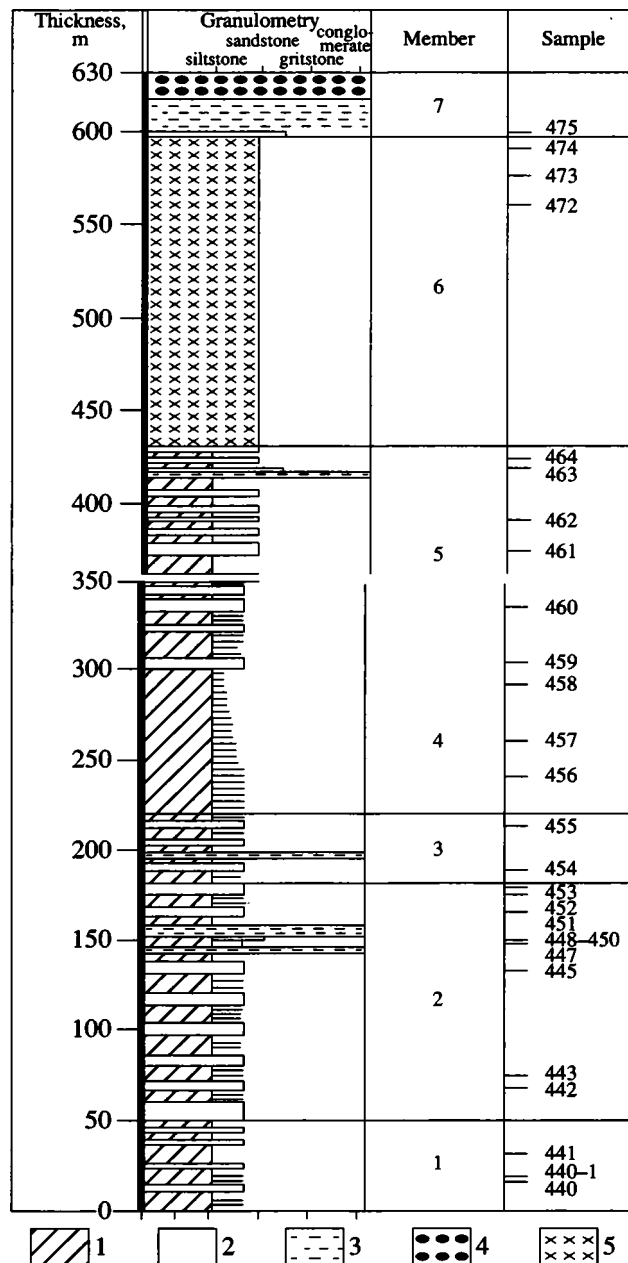


Fig. 2. The Povorotnyi Cape flysch section. (1) Silty mudstones and siltstones; (2) sandstones; (3) slump deposits; (4) polymictic olistostrome; (5) crushed boudins of mudstones, siltstones, and sandstones.

with laminated (a few millimeters thick) medium- and coarse-grained sandstones (Fig. 3).

Member 3 (180–220 m) represents a transition from sandy flysch of Member 2 to finer flysch of Member 4. As compared with Member 2, sandstones of Member 3 show greater variability in lamination types: thin horizontal, flat-wavy, and intermittent cross-wavy ones. Sand 1–10-cm-thick dikes that cut the rocks transversely to bedding are observed. There is a 2.5-m-thick flysch stratum with slump structures that is similar in

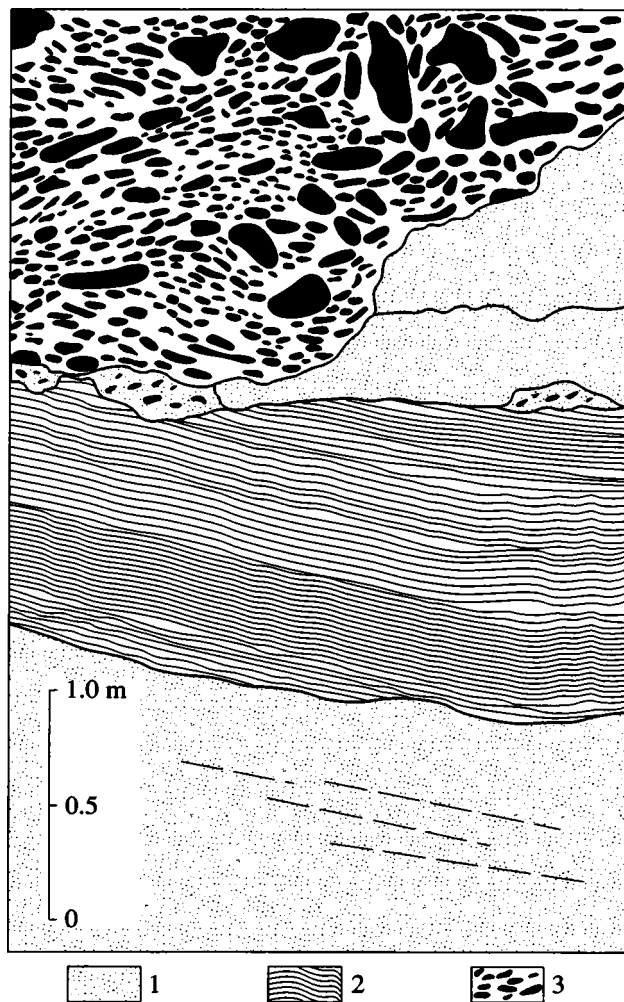


Fig. 3. Relationships between massive and laminar sandstones and strata with slump structures (drawing after photograph). (1) Massive sandstones; (2) laminar sandstones; (3) slump deposits.

structure and composition to analogous strata of Member 2. Large silty mudstone fragments are rare; when present, they are up to 1 m long (the average length of flattened clasts is 5–20 cm).

Member 4 (220–300 m) is represented by rhythmically layered silty-sandy flysch with a bed thickness of 5–10 cm and a sandstone/siltstone ratio of 1 : 1. Fine pelitic material is rare. Sandstones are fine- and medium-grained; rare thin (3–5 cm) gritstone beds occur. Upsection, the decrease in sandstone interlayer thickness and, simultaneously, in grain size is observed. Deposits are characterized by peculiar flysch structures: obscure thin discontinuous cross lamination in sandstones, intermittent flat-wavy lamination in the sandstone-siltstone transition level (the element *c* of the Bouma cycle), horizontal lamination in siltstones and mudstones, and convolute dislocations in sandstones.

Member 5 (300–430 m) is similar in structure to Member 2. Thick (5–7 m) layers of massive sandstones occur among horizontally bedded siltstones, sandstones, and mudstones. The main difference from this member is in the presence of well-expressed whirlpool holes at the base of thick sandstone beds. The paleocurrent azimuth (based on the orientation of whirlpool holes) is 286° – 288° .

Member 6 (430–600) is composed of cataclastic silty mudstones with sandstone boudins (from 5–10 cm to large blocks) and bed fragments up to 1 m thick. Well-expressed “classic” turbidites with sandstone and siltstone (about 10 cm thick) are confined to the contact of this member with the underlying coarse deposits of Member 5.

Two siliceous-clayey strata occur in the member. The lower one (about 3 m) is strongly dislocated. In the upper one (about 10 m), relic lamination and two thin (15 cm) silicilith beds are observed at the base.

Member 7 (600–630 m) comprises two strata of slump deposits. The lower stratum is similar to counterparts in underlying members. It has an erosional contact with the underlying thin (up to 1.3 m) wedging out deposits with fine-rhythmic lamination. The upper stratum represents olistostrome with diverse well-rounded flattened pebbles of effusive, intrusive (?), and volcanogenic-sedimentary rocks. The olistostrome matrix is coarse-grained, sandy, and polymictic.

The sequence structure of the Povorotnyi Cape flysch reflects significant variations in hydrodynamics of depositional environments. Members of fine- and medium-rhythmic flysch that prevail in the section accumulated under the clastic material discharge from turbidity flows of medium and low density, as evidenced by structures characteristic of facies of submarine fan lobes. The presence in the section of separate thick sandstone beds reflects the incidental emergence in the past of highly dynamic conditions for the clastic material transportation. The absence of graded sorting in thick beds is typical of environments affected by high-density grain flows, i.e., facies of distribution systems (Hein, 1982). Strata with slump structures in flysch were formed at the expense of high-concentration suspension flows, within which conditions for the mixing and the selective orientation of elongated particles in parallel to the flow direction existed. The presence of oval-elongated inclusions in the sandy-silty matrix reflects weak lithification of sediments involved in the flow. The relatively common occurrence of such deposits in the section indicates the frequency of this phenomenon in the considered depositional realm. The compositional similarity of the clastic material in slump strata and host rocks suggest a local source. The minor thickness of slump strata testifies to the small volume of the material involved in the paste-like flow, insignificant distance of its transportation, and flat relief. The formation of slump strata may be related to local avalanche processes, for example, due to the ero-

Table 1. Petrographic composition of sandstones (%)

Unit	Sample no.	Q	F	L
Myalekasyn	402	1	2	97
	404	1	2	97
	407	1	1	98
	409	4	6	90
	410	7	10	83
	412	2	4	94
	413	1	5	94
	414	1	4	95
	415	1	5	94
	Average	2	4	94
Lagernyi	433	3	37	60
	437	1	35	64
	438	2	42	56
	479	5	46	49
	Average	3	40	57
Lagernyi flysch	490	29	43	28
	491	26	44	30
	493	23	49	28
	511	25	46	29
	Average	26	45	29
Povorotnyi Cape flysch	442	31	46	23
	443	27	47	26
	444	33	44	23
	445	35	43	22
	447	38	42	20
	448	30	39	31
	451	29	44	27
	453	30	41	29
	460	28	44	28
	461	28	42	30
	462	30	44	26
	464	33	42	25
	465	26	39	35
	466	34	30	36
	Average	31	42	27

sion and collapse of the distributor-channel walls. The invariably distinct erosional contact with underlying deposits reflects the sufficiently high energy of flows.

Fine-stratified deposits are probably related to the bottom current activity. This is evidenced by lamination and absence of the pelitic material, typical gradual transitions from medium- to coarse-grained sandstones, fractionation of dark-colored minerals, and large dimensions of the clastic material. As a rule, these deposits occur directly below slump strata and, thus,

have an erosional contact with the overlying strata. It is probable that bottom currents had a pronounced abrasive effect on the channel side and provoked caving.

MINERALOGIC AND PETROGRAPHIC COMPOSITION

Studies of mineralogic and petrographic composition revealed significant differences between Lagernyi and Myalekasyn sandstones and flysch sandstones.

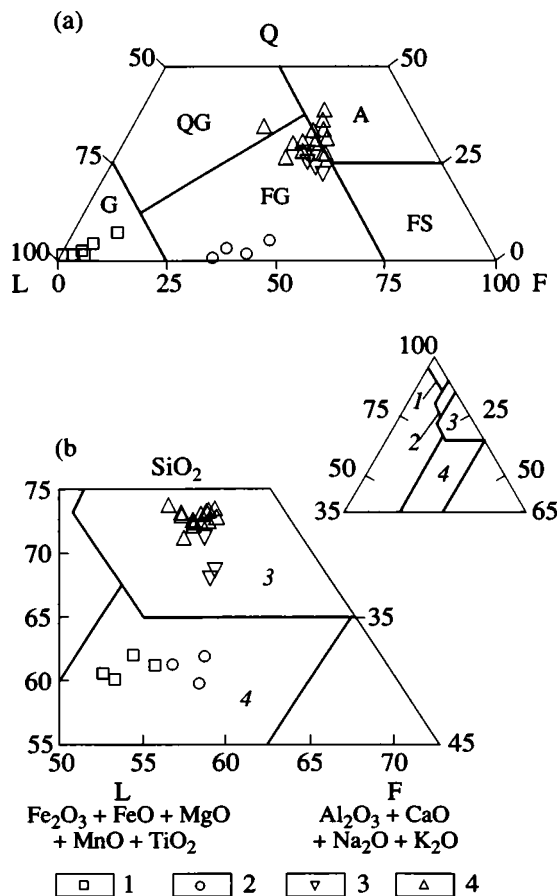


Fig. 4. Ternary diagrams of sandstone composition. (a) Petrographic composition (%): (Q) quartz; (L) lithoclasts; (F) feldspars. Fields (after Shvanov, 1987): (G) graywackes; (QG) quartz graywackes; (FG) feldspar graywackes; (A) arkoses; (FS) feldspar sandstones. (b) Petrochemical composition (wt %), sandstone fields (Kossovskaya and Tuchkova, 1988): (1) monomictic; (2) oligomictic; (3) polymictic; (4) volcanomictic.

Units: (1) Myalekasyn; (2) Lagernyi; (3) Lagernyi flysch; (4) Povorotnyi Cape flysch.

Table 1 presents the results of the petrographic analysis of sandstones.

Myalekasyn and Lagernyi sandstones are mainly composed of clasts of intermediate and basic effusives with an admixture of pyroclastic material. In general, vitroclastic tuffs and tuffites are common among psammites. Clasts in sandstones are represented by basalts with various structures, andesites, gabbroids, diabases, siliciliths, microquartzites, siliceous-clayey shales, basic chloritized glass, and, less commonly, by metamorphic rocks. On the ternary diagram of distribution of main rock-forming components (Fig. 4a), data points of Myalekasyn and Lagernyi sandstones are close to the LF side that is characteristic of environments which are lacking the terrigenous material influx.

In Myalekasyn sandstones, rock clasts sharply dominate over quartz and feldspar grains, and on the QLF

diagram, data points are grouped in the graywacke field (Fig. 4a). Feldspars are mostly represented by basic and intermediate plagioclases (andesine and labradorite). Among other minerals, clinopyroxene and amphiboles are common. Quartz grains are rare. The fragment of polymictic sandstone similar to flysch sandstone was observed in one thin section of the Myalekasyn sandstone. Clasts are poorly sorted, angular, and closely packed; cement is minor. The formula of the average contents of quartz, feldspar, and lithoclasts is as follows: $Q_{24}F_{44}L_{94}$ (Table 1).

As compared with Myalekasyn sandstones, the Lagernyi sandstones are characterized by the increase of the main rock-forming component (feldspar), relative decrease in the rock clast share; data points in the latter case tend to the base of the feldspar graywacke field (Fig. 4a). Lagernyi sandstones are particularly rich in pyroclastic material. Andesitic and basaltic tuffs with various combinations of vitro-, crystallo-, and lithoclastic constituents are common. Feldspar and quartz clasts also show features of pyroclastic origin. Feldspars are splintery, broken along cleavage planes, split, fused, and occasionally euhedral. A few quartz grains are splintery, crescent-shaped, and sometimes rounded. As a whole, Lagernyi deposits are distinguished from Myalekasyn unit first, by well-pronounced cataclastic structures and milonitization and second, by a wider spectrum of composing rocks.

Effusive rocks are represented by cataclastic aphyric basalts often transformed into epidote-sericite-chlorite and epidote-chlorite-actinolite schists. Some boudins contain basalts and olivine-pyroxene diabases.

Carbonate bed boudins are composed of sparite and microsparite crystalline limestone with separate small quartz grains along with veinlets and small lenses of secondary microquartzite. The milonitization zone carbonates contain abundant large quartz grains with wavy extinction, their massive aggregates, and mosaic microquartzites in fissures.

Siliceous rocks, which are subjected to cataclasis, commonly contain traces of recrystallized and dissolved radiolarians. Bright-red jaspers are intensely recrystallized into the form of microquartzites, and then carbonatized and chloritized. Sometimes, dolomite occurs in the siliceous matrix.

Flysch unit sandstones are characterized by the sharp decrease of rock clasts and increase of mineral grains. Sandstone data points are close to the transition between feldspathic graywacke and arkose fields (Fig. 4a), which emphasizes the relatively higher mineralogical maturity of flysch sandstones as compared to Myalekasyn and Lagernyi counterparts. In quantitative ratios of main rock-forming components, flysch sandstones from the Lagernyi and Povorotnyi Cape are similar (Table 1) and characterized by the following composition: $Q_{26}F_{45}L_{29}$ and $Q_{31}F_{42}L_{27}$, respectively.

Clasts are mostly represented by quartz (about 30%), acidic plagioclases (mainly oligoclase), potas-

Table 2. Results of silicate (wt %) and quantitative spectral (ppm) analyses and main petrochemical coefficients

Components	Myalekasyn unit, sample no.					Lagermyi unit, sample no.				Lagermyi flysch, sample no.			
	412	413	414	415	average	431	432	479	average	490	491	511	average
SiO ₂	57.08	57.25	58.50	59.38	58.05	59.48	58.37	57.30	58.38	69.40	65.66	67.71	67.59
TiO ₂	1.12	1.07	1.02	1.00	1.05	1.09	1.02	1.17	1.09	0.63	0.63	0.67	0.64
Al ₂ O ₃	12.90	12.63	13.82	13.44	13.20	16.72	16.40	17.02	16.71	14.16	14.72	15.16	14.68
Fe ₂ O ₃	2.62	1.65	0.84	2.64	1.94	1.16	1.23	1.49	1.29	0.98	1.24	1.8	1.34
FeO	5.63	5.89	5.52	4.83	5.47	5.02	6.49	5.8	5.77	2.84	3.2	2.03	2.69
MnO	0.04	0.05	0.08	0.10	0.07	0.06	0.14	0.12	0.11	0.01	0.06	0.06	0.04
CaO	5.55	4.75	5.13	4.73	5.04	3.72	3.77	4.72	4.07	1.68	3.25	2.84	2.59
MgO	6.41	7.56	5.58	5.35	6.23	2.60	3.13	2.68	2.80	0.91	1.39	1.49	1.26
Na ₂ O	2.88	2.82	4.15	3.37	3.31	5.70	3.06	4.46	4.41	4.15	4.15	4.88	4.39
K ₂ O	0.78	0.90	1.00	0.91	0.90	0.54	1.84	1.20	1.19	2.40	1.90	1.72	2.01
P ₂ O ₅	0.15	0.15	0.16	0.16	0.16	0.19	0.28	0.28	0.25	0.09	0.13	0.10	0.11
Co ₂	0.90	0	0	1.00	0.48	0.80	0	0.65	0.48	0	0.55	0	0.18
L.O.I.	3.62	4.67	3.69	2.81	3.70	2.76	4.19	2.55	3.17	2.20	2.74	1.30	2.08
Total	99.68	99.39	99.49	99.72		99.84	99.92	99.44		99.45	99.62	99.76	
Cr	220.0	195.0	200.0	175.0	197.50	37.0	20.0	27.0	28.00	37.0	40.0	40.0	39.00
Ni	120.0	120.0	115.0	110.0	116.25	28.0	20.0	23.0	23.67	27.0	28.0	25.0	26.67
V	140.0	135.0	150.0	125.0	137.50	140.0	110.0	140.0	130.00	60.0	90.0	65.0	71.67
Cu	40.0	60.0	45.0	35.0	45.00	29.0	35.0	29.0	31.00	12.0	17.0	12.0	13.67
Co	20.0	20.0	20.0	18.0	19.50	15.0	12.0	16.0	14.33	8.0	9.0	8.0	8.33
Pb	5.0	5.0	3.0	7.0	5.00	7.0	17.0	7.0	10.33	25.0	22.0	19.0	22.00
Ga	16.0	14.0	15.0	15.0	15.00	19.0	20.0	18.0	19.00	18.0	20.0	18.0	18.67
Ge	1.2	1.0	1.1	1.0	1.08	1.1	1.2	1.1	1.13	1.0	1.0	1.0	1.00
Zn	90.0	95.0	85.0	90.0	90.00	100.0	120.0	110.0	110.00	70.0	70.0	60.0	66.67
Sn	1.4	1.4	1.3	1.2	1.33	1.7	2.0	1.4	1.70	1.3	1.4	1.3	1.33
B	22.0	17.0	28.0	30.0	24.25	16.0	55.0	23.0	31.33	40.0	45.0	17.0	34.00
Fe' + Mg	15.29	15.76	12.55	13.36	14.24	9.34	11.57	10.62	10.51	5.05	6.19	5.55	5.59
(Fe' + Mg/Al)	1.19	1.25	0.91	0.99	1.08	0.56	0.71	0.62	0.63	0.36	0.42	0.37	0.38
Si/Al	4.42	4.53	4.23	4.42	4.40	3.56	3.56	3.37	3.49	4.90	4.46	4.47	4.61
K/Na	0.27	0.32	0.24	0.27	0.28	0.09	0.60	0.27	0.32	0.58	0.46	0.35	0.46
(K + Na/Al)	0.28	0.29	0.37	0.32	0.32	0.37	0.30	0.33	0.33	0.46	0.41	0.44	0.44
Al/Na	4.48	4.48	3.33	3.99	4.07	2.93	5.36	3.82	4.04	3.41	3.55	3.11	3.36
Mg/Ca	1.15	1.59	1.09	1.13	1.24	0.70	0.83	0.57	0.70	0.54	0.43	0.52	0.50

sium feldspar (often microcline), and biotite. Lenses of coalified and commonly, pyritized plant debris occur. Muscovite, sphene, garnet, hornblende, and clinopyroxene are also observed. Quartz is often fractured and mosaic (with wavy extinction). Some grains bear euhedral zircon and apatite crystals.

Rock clasts are represented by cherts, acidic and basic volcanics, microgranites, mudstones, siltstones, tuffites, quartz-micaceous schists, basalts, andesites, and organo-

genic carbonate. In flattened clayey-siliceous inclusions, abundant radiolarians can sometimes be observed.

Rocks are characterized by the presence of interstitial and pore cement, but conform cement-free structure is also observed. In composition, cement is sandy (quartz and feldspar grains plus cherty and volcanic clasts), siliceous-micaceous, and carbonate. The grain packing is good, and sorting is medium. As a rule, clasts are acute-angled, unrounded, and sometimes semirounded.

Table 2. (Contd.)

Components	Povorotnyi Cape flysch														
	442	444	445	447	448	449	450	451	453	459	460	461	462	464	ave- rage
SiO ₂	71.37	71.45	71.07	70.60	69.78	71.59	69.05	69.61	71.13	70.62	69.56	69.96	70.98	70.51	70.52
TiO ₂	0.85	0.42	0.42	0.51	0.43	0.46	0.56	0.53	0.54	0.64	0.62	0.53	0.60	0.70	0.56
Al ₂ O ₃	12.75	14.25	13.86	13.09	13.23	11.72	14.02	13.84	13.29	12.82	13.48	13.83	13.42	12.56	13.3
Fe ₂ O ₃	1.8	1.03	0.76	0.4	0.44	2.62	2.52	0.86	2.26	2.23	1.53	0.84	1.34	1.25	1.42
FeO	2.48	1.66	2.23	2.43	3.46	2.09	2.25	1.7	1.47	1.87	2.03	1.91	1.4	2.5	2.11
MnO	0.03	0.03	0.01	0.06	0.01	0.03	0.02	0.04	0.03	0.05	0.03	0.03	0.02	0.02	0.03
CaO	1.72	1.34	1.58	2.52	1.74	2.11	1.51	2.27	1.87	1.44	2.38	2.01	1.89	2.02	1.89
MgO	0.99	0.81	1.14	1.48	1.50	1.34	1.54	1.63	1.25	1.24	1.11	0.73	1.07	1.17	1.21
Na ₂ O	4.64	4.52	4.27	4.15	3.91	3.49	3.31	4.15	4.09	4.27	3.85	4.21	4.09	4.40	4.10
K ₂ O	1.63	2.12	2.14	1.76	2.56	2.09	2.63	1.94	2.40	1.84	1.76	2.40	2.40	2.40	2.15
P ₂ O ₅	0.08	0.12	0.05	0.07	0.05	0.03	0.05	0.03	0.07	0.08	0.09	0.01	0.09	0.11	0.07
Co ₂	0	0	0	0.55	0	0.50	0	0	0	0	0.40	0	0	0	0.10
L.O.I.	1.90	1.77	1.97	1.21	2.57	2.49	2.26	2.90	2.03	2.26	2.52	2.22	1.95	1.74	2.13
Total	100.24	99.52	99.50	98.83	99.68	100.56	99.72	99.50	100.43	99.36	99.36	98.68	99.25	99.38	
Cr	30.0	33.0	33.0	35.0	35.0	37.0	40.0	37.0	40.0	33.0	37.0	37.0	40.0	47.0	36.71
Ni	27.0	24.0	22.0	22.0	30.0	30.0	30.0	27.0	27.0	27.0	28.0	24.0	23.0	30.0	26.5
V	45.0	40.0	45.0	50.0	55.0	50.0	60.0	35.0	60.0	50.0	55.0	50.0	55.0	60.0	50.71
Cu	9.0	9.0	9.0	10.0	17.0	12.0	17.0	10.0	10.0	12.0	12.0	10.0	9.0	10.0	11.14
Co	8.0	7.0	6.0	8.0	9.0	9.0	9.0	8.0	8.0	7.0	8.0	7.0	7.0	7.0	7.71
Pb	28.0	27.0	25.0	25.0	29.0	35.0	29.0	30.0	25.0	25.0	24.0	24.0	22.0	23.0	26.5
Ga	16.0	19.0	19.0	18.0	16.0	16.0	19.0	20.0	19.0	17.0	20.0	19.0	16.0	17.0	17.93
Ge	1.0	0	0	0	1.0	1.0	1.0	1.0	1.0	0	0	0	0	0	00.43
Zn	80.0	95.0	55.0	50.0	65.0	55.0	70.0	70.0	60.0	70.0	80.0	65.0	58.0	65.0	67
Sn	1.3	1.2	1.3	1.2	1.0	1.2	1.3	1.4	1.4	1.3	1.3	1.2	1.3	1.3	1.26
B	30.0	35.0	32.0	35.0	37.0	32.0	48.0	30.0	30.0	32.0	32.0	30.0	25.0	25.0	32.36
Fe' + Mg	5.55	3.68	4.38	4.58	5.79	6.28	6.56	4.38	5.14	5.55	4.90	3.69	3.97	5.20	4.97
(Fe' + Mg)/Al	0.44	0.26	0.32	0.35	0.44	0.54	0.47	0.32	0.39	0.43	0.36	0.27	0.30	0.41	0.38
Si/Al	5.60	5.01	5.13	5.39	5.27	6.11	4.93	5.03	5.35	5.51	5.16	5.06	5.29	5.61	5.32
K/Na	0.35	0.47	0.50	0.42	0.65	0.60	0.79	0.47	0.59	0.43	0.46	0.57	0.59	0.55	0.53
(K + Na)/Al	0.49	0.47	0.46	0.45	0.49	0.48	0.42	0.44	0.49	0.48	0.42	0.48	0.48	0.54	0.47
Al/Na	2.75	3.15	3.25	3.15	3.38	3.36	4.24	3.33	3.25	3.00	3.50	3.29	3.28	2.85	3.27
Mg/Ca	0.58	0.60	0.72	0.59	0.86	0.64	1.02	0.72	0.67	0.86	0.47	0.36	0.57	0.58	0.66

Fine-grained varieties are represented by silty mudstones, siliceous mudstones with recrystallized and semidissolved, sometimes well-preserved radiolarians, and carbonaceous siltstones. These varieties sometimes bear fragments and whole bivalve and brachiopod shells and, less commonly, separate brachiopod needles.

In the Povorotnyi Cape flysch, the share of andesite, basalt, and crystalloclastic tephra clasts increases upsection. Homogeneous andesite lithoclasts and brown fresh glass appear. The presence of the latter suggests sedimentation to proceed synchronously with explosions.

WHOLE-ROCK COMPOSITIONS OF SANDSTONES

Table 2 presents the results of the chemical analysis of various sandstones and their main coefficients.

The highest average values of a sum of mafic oxides $\text{Fe}_2\text{O}_{3(\text{tot})}^1 + \text{MgO}$ and their ratio to Al_2O_3 , i.e., $\text{Fe}_2\text{O}_{3(\text{tot})} + \text{MgO}/\text{Al}_2\text{O}_3$, are characteristic of the Myalekasyn sandstones (14.24 and 1.08, respectively), whereas the

¹ The total iron content $\text{Fe}_2\text{O}_{3(\text{tot})} = \text{FeO} \cdot 1.1114 + \text{Fe}_2\text{O}_3$.

lowest values are typical of the flysch unit sandstones (5.59 and 0.38, respectively).

In the Myalekasyn and Lagernyi sandstones, the quartz content does not exceed 1–3%. The SiO_2 content is 58.05% in Myalekasyn sandstones and 58.38% in Lagernyi sandstones. The $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio in sandstones from both these units is similar and makes up 0.28 and 0.32, respectively. These data allow Myalekasyn and Lagernyi sandstones to be classified as graywackes impoverished in quartz, according to the Crook (1972) classification. Sandstones from the flysch unit correspond, by the same parameters, to the group of graywackes with the intermediate quartz content. The Lagernyi and Povorotnyi Cape flysch deposits contain 26 and 31% of quartz and 67.59 and 70.52% of SiO_2 , respectively. The $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio in these rocks amounts to 0.46 and 0.53, respectively.

The $\text{K}_2\text{O} + \text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio is commonly higher in mature sandstones than in graywackes (Middleton, 1960). In unit the flysch sandstones, the values of this ratio (0.44 in Lagernyi and 0.47 in Povorotnyi Cape) exceed those for the Myalekasyn (0.32) and Lagernyi (0.33) sandstones.

On the ternary diagram proposed by Kossovskaya and Tuchkova (1988) for psammite classification by the ratio of main oxides, Myalekasyn and Lagernyi sandstones fall into the field of volcanomictic rocks, whereas the flysch unit sandstones, occur in the field of polymictic rocks (Fig. 4b).

On binary diagrams by (Bhatia, 1983), which allow the geodynamic depositional conditions to be interpreted, Myalekasyn and Lagernyi sandstones are close to the ensimatic island-arc fields, whereas the flysch unit sandstones never fall into this field and are grouped in fields of ensialic arcs and active margins (Fig. 5).

DISCUSSION

The data presented here show that structural and compositional rock complexes of different age and different geodynamic settings are juxtaposed in the Vitatglya River to Povorotnyi Cape area of the Penzhina–Anadyr fold system.

Jurassic–Cretaceous Kingiveem siliceous–basaltic deposits represent fragments of oceanic crust, which is evidenced by compositions typical of oceanic tholeiite basalts and by deepsea patterns of siliceous deposits.

Middle Jurassic–Lower Cretaceous terrigenous flysch deposits accumulated at the expense of clastic material from the active continental margin, as evidenced by sandstone composition. Taking into consideration results of paleocurrent direction estimates based on bottom marks and reconstructing the normal bed position (assuming that no significant rotation of the flysch block has occurred), it can be suggested that the sedimentary material was transported from the northwest.

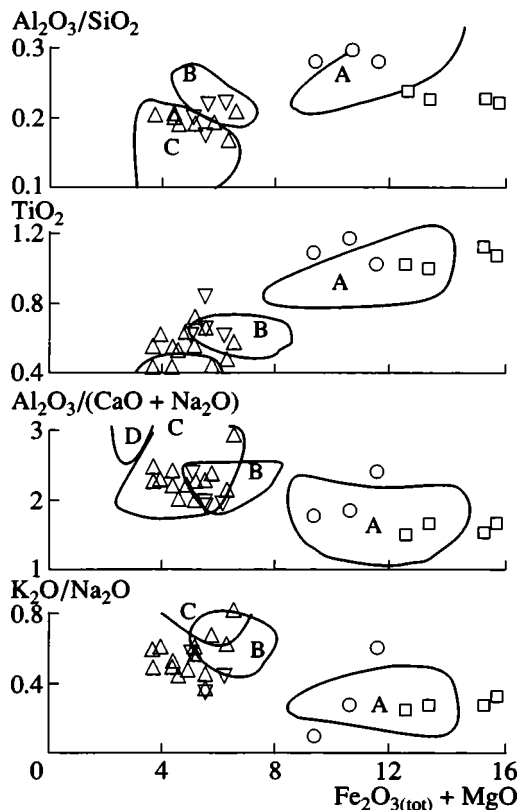


Fig. 5. Diagrams of geodynamic typification (after Bhatia, 1983) Volcanic arcs: (A) ensimatic, (B) ensialic; continental margins: (C) active, (D) passive. Total iron content $\text{Fe}_2\text{O}_3(\text{tot}) = \text{FeO} \cdot 1.1114 + \text{Fe}_2\text{O}_3$. For other symbols see Fig. 4.

The structural and lithological complexes of the Koni–Taigonos fold system, located northwestward of the recent structure of the peninsula, are considered the Taigonos segment of the Jurassic–Early Cretaceous Uda–Murgal ensialic volcanic arc. Although the spatial position of the Uda–Murgal arc in the Jurassic–Early Cretaceous is unclear, it seems probable that it was a part of the continental margin.

Composition and structure of the flysch unit allow us to reconstruct the following succession of events accompanying its formation. The sedimentary material was mobilized in the subaerial continental setting, which is evidenced by the presence of coalified plant remains in sandstones. The further alluvial transportation of the clastic material to the main erosion base line favored its higher mineralogical maturity. When crossing the subaerial volcanism area (Uda–Murgal arc?), the clastic material became enriched in volcanogenic components. Sediments were transported by submarine turbidity flows into the deepsea areas zone and discharged at the sea floor, resulting in the formation of a submarine fan. The structural pattern of the Povorotnyi Cape flysch section allows us to reconstruct the sufficiently mature elongated submarine fan with one main feeding channel.

Similar elongated fans extending over a distance of hundreds of kilometers are particular for continental margins that are characterized by the slope with a developed equilibrium profile (Shanmugam *et al.*, 1988).

The clastic material influx from the active margin occurred at least since the Middle Jurassic and continued to the Early Neocomian as evidenced by the composition and age of flysch deposits. The composition of Middle–Upper Jurassic sandstones from Lagernyi flysch deposits suggests the relative temporal stability of this source. However, the tectonic regime in the accumulation zone had been changing.

Therefore, in the Middle–Late Jurassic, the subarkose clastic material accumulated above siliceous–basaltic oceanic rocks that is reflected in the contact pattern between Povorotnyi Cape flysch deposits and Kingiveem siliceous–basaltic rocks. It is reasonable to assume that the oceanic plate directly adjoined the continental margin thus allowing the relatively mature polymictic clastic material to penetrate easily into the deep part of the basin and take part in the formation of sedimentary cover over an oceanic plate.

In the Late Jurassic–Neocomian, similar polymictic (subarkose) clastic material transported from the active continental margin entered the zone of submarine island-arc volcanism that is evidenced by the alternation of pillow-basalts and hyaloclastites of the effusive unit and terrigenous sequences incorporating polymictic sandstones.

The available data do not allow paleomorphology of the Jurassic–Early Cretaceous zone of island-arc volcanism to be unambiguously interpreted. It is reasonable to suggest that at least since the Late Jurassic, the active ensimatic arc was partially adjoined to the continental margin and that morphologically significant barriers in the transportation way of the clastic material from the active continental margin did not exist. In the zone of ensimatic volcanism, fissure lava extrusions probably occurred without formation of morphologically pronounced rises.

Significant relief differentiation probably occurred in the post-Valanginian time at the terminal stage of island-arc volcanism. This favored accumulation of Lagernyi coarse-clastic slump deposits and also resulted in the appearance of the morphological barrier that hindered the clastic material influx from the active margin.

The influence of the active margin could continue in the time interval, when Lagernyi deposits accumulated. Indeed, Lagernyi sandstones somewhat differ from exclusively graywacke-type Myalekasyn sandstones in the greater amount of feldspars (on ternary diagrams, their compositions are grouped in the lower sector of the feldspar graywacke field), relative reduction in the clasts rock, and relative enrichment in pyroclastic material. Marmorized limestones in Lagernyi deposits were probably of local origin. Previously, the presence of oceanic guyot fragments was noted in the Kuyul

massif sections (*Kuyul'skii* ..., 1990). In the Lagernyi unit section along the considered cross section, no distinct correlation between recrystallized limestones and basalts was observed. Besides, up to the present, there has been no evidence of the presence in the section of oceanic intraplate basalts characteristic of guyots.

Solely volcanomictic Hauterivian–Barremian sandstones of the Myalekasyn Formation bear the signs of the monostage and fast burial. High dynamics of transporting flows, poor sorting of the coarse-grained clastic material, sharply subordinate role of the lutite material, and presence of amalgamated sandstones suggest deposition of the considered part of the Myalekasyn Formation to be related to the nonmature submarine fan at the paleoslope base not far from the provenance. Similar environments are characteristic of interarc and near-arc flanks of fore-arc basins.

Activation of island-arc volcanism along with changes in structural and morphological patterns in the Hauterivian–Barremian could be caused by the commencement of collision between the ensimatic island arc and active continental margin that marked the termination of the Jurassic–Early Cretaceous evolution of this segment of the Asian eastern continental margin.

CONCLUSION

Based on this study, the following conclusions may be drawn:

(1) Two contrasting clastic material sources of different ages that influenced accumulation of sedimentary rock complexes were established.

The first source was active since the Middle Jurassic to Early Cretaceous and represented an active continental margin, which probably comprised the sialic Uda–Murgal volcanic chain. Middle–Upper Jurassic Povorotnyi Cape and Upper Jurassic–Lower Neocomian Lagernyi flysch deposits were formed under the influence of this source.

The ensimatic island arc that existed until the Hauterivian–Barremian served as the second source of the clastic material. Deposition of volcanomictic Lagernyi and Myalekasyn graywackes is related to this source.

(2) In the Middle–Late Jurassic (Callovian), there was a sector along the convergence zone, where the oceanic plate was next to the continental margin, and subarkose material could easily enter the deep part of the ocean. In the Late Jurassic–early Neocomian, similar material accumulated together with products of the active ensimatic island arc.

(3) Activation of island-arc volcanism in the post-Valanginian time resulted in the relief differentiation. This favored the accumulation of coarse-clastic slump deposits of Lagernyi and Myalekasyn sequences. Structural reorganization could form the morphologic barrier that hindered the clastic material influx from the active margin.

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REFERENCES

- Bhatia, M.R., Plate Tectonics and Geochemical Composition of Sandstones, *J. Geol.*, 1983, vol. 91, pp. 611-627.
- Chekhov, A.D., Tectonics of the Talaya-Pekul'nei Zone, in *Ocherki tektoniki Koryakskogo nagor'ya* (Essays on Tectonics of the Koryak Highland), Moscow: Nauka, 1982, pp. 70-106.
- Chekhov, A.D. and Palandzhyan, S.A., New Data on Geological Structure of the Taigonos Peninsula, *Geol. Geologorazv.*, 1994, no. 4, pp. 7-11.
- Crook, K.A.W., Lithogenesis and Geotectonics: The Significance of Compositional Variation in Flysch Arenites (Graywackes), in *Modern and Ancient Geosyncline Sediments*. Proc. Symp. Madison (Wisc.) Tulsa (Okla), 1972, pp. 304-309.
- Gel'man, M.L. and Nekrasov, G.E., Mesozoic Eclogites of the Taigonos Peninsula, *Geol. Geofiz.*, 1968, no. 12, pp. 32-40.
- Hein, F.J., Depositional Mechanisms of Deepsea Coarse Clastic Sediments, Cap Enrage Formation, Quebec, *Can. J. Earth Sci.*, 1982, vol. 19, pp. 267-287.
- Kossovskaya, A.G. and Tuchkova, M.I., Problem of Mineralogical and Petrochemical Classification of Sandstones, *Litol. Polezn. Iskop.*, 1988, no. 2, pp. 8-24.
- Kuyul'skii ofiolitovyi terrein* (The Kuyul Ophiolite Terrain), Sokolov, S.D. and Khanchuk, A.I., Eds., Vladivostok: Dal'nevost. Otd. Akad. Nauk SSSR, 1990.
- Livshits, I.L., Two Stages of Regional Metamorphism of Rocks in the Northern Taigonos Peninsula, *Dokl. Akad. Nauk SSSR*, 1972, vol. 205, no. 6, pp. 1432-1435.
- Middleton, G.V., Chemical Composition of Sandstones, *Bull. Geol. Soc. Am.*, 1960, vol. 71, no. 7, pp. 1011-1026.
- Nekrasov, G.E., *Tektonika i magmatizm Taigonosa i Severo-Zapadnoi Kamchatki* (Tectonics and Magmatism of the Taigonos Peninsula and Northwestern Kamchatka), Moscow: Nauka, 1976.
- Nekrasov, G.E., Zaborovskaya, N.B., and Gel'man, M.L., Tectonics of the Transition Zone Between Mesozooids and Structures of the Koryak-Kamchatka Fold Belt with the Taigonos Peninsula as an Example, in *Mezozoiskii tektogenez* (Mesozoic Tectogenesis), Magadan: Dal'nevost. Nauch. Tsentr, Akad. Nauk SSSR, 1970, pp. 80-86.
- Shanmugam, G., Moiola, R.J., McPherson, J.G., and O'Connell, S., Comparison of Turbidite Facies in Modern Passive-Margin Mississippi Fan with Ancient Active-Margins Fans, *Sediment. Geol.*, 1988, vol. 58, no. 1, pp. 63-77.
- Shvanov, V.N., *Petrografiya osadochnykh porod* (Sedimentary Petrography), Leningrad: Nedra, 1987.
- Sokolov, S.D., *Akkretionnaya tektonika Koryaksko-Kamchatskogo segmenta Tikhookeanskogo poyasa* (Accretional Tectonics of the Koryak-Kamchatka Segment of the Pacific Belt), Moscow: Nauka, 1992.
- Walker, R.G., Deposition of Mesozoic Resedimented Conglomerates and Associated Turbidites in Southwestern Oregon, *Geol. Soc. Am. Bull.*, 1977, vol. 88, pp. 273-285.
- Zaborovskaya, N.B., *Vnutrennyaya zona Okhotsko-Chukotskogo vulkanogenogo poyasa na Taigonose* (The Inner Zone of the Okhotsk-Chukotka Volcanogenic Belt in the Taigonos Peninsula), Moscow: Nauka, 1978.
- Zaborovskaya, N.B. and Nekrasov, G.E., Tectonics and Magmatism of the Transition Zone Between Yana-Kolyma Mesozooids and Koryak-Kamchatka Fold Belts, *Geotektonika*, 1977, no. 1, pp. 103-117.
- Zagruzina, I.A. and Smirnov, V.N., The Age of Magmatic and Metamorphic Rocks of the Taigonos Peninsula, in *Magmatizm Severo-Vostoka SSSR* (Magmatism of the Northeast USSR), Moscow: Nauka, 1973, pp. 219-224.
- Zhulanova, I.L., Tectonics and Evolution of Metamorphic Complexes of the Northern Taigonos Peninsula, *Geotektonika*, 1974, no. 1, pp. 111-122.
- Zhulanova, I.L., Geology of the Verkhnepylgin Complex and Some Peculiarities of Young Metamorphism in the Marginal Zone of the Taigonos Massif, in *Magmatizm Severo-Vostoka Azii* (Magmatism of the Northeast Asia), Magadan: Knizhnoe Izd-vo, 1975a, part 2, pp. 112-118.
- Zhulanova, I.L., Origin and Age of Metamorphic Rocks of the Northern Taigonos Peninsula, in *Materialy po geologii i poleznym iskopaemym Severo-Vostoka SSSR* (Materials on Geology and Mineral Resources of the Northeast USSR), Magadan: Knizhnoe Izd., 1975b, issue 21, pp. 55-62.
- Zhulanova, I.L., *Zemnaya kora Severo-Vostoka Azii v dokembrii i fanerozoie* (The Northeast Asian Crust in the Precambrian and Phanerozoic), Moscow: Nauka, 1990.

Phosphorite Formation as a Development Stage of the Carbonate Platform in Lesser Karatau

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Abstract—The paper considers different stages of carbonate platform formation in the Karatau Range, Kazakhstan during the Precambrian and Lower Paleozoic. It is shown that the leveling of bottom relief of the Chulaktau paleobasin occurred due to the growth of biohermal carbonate–hyaline buildups and was complicated by a transgression of hydrosulfuric basin, whose waters contained excessive quantities of dissolved silica, phosphorus, and manganese. As a result of the elimination of anoxic conditions in the paleosea littoral zone, carbonate and carbonate–hyaline bioherms were substituted by phosphorus and silica, which, in its turn, led to the subsequent formation of layers and lenses of pelletal phosphorites.

EVOLUTION OF THE RIPHEAN–LOWER PALEOZOIC PALEOBASIN IN KARATAU

During the Precambrian–Lower Paleozoic geological history of the phosphorite-bearing basin in Lesser Karatau, the following three stages can be quite clearly distinguished.

The first stage covers the Riphean–Early Vendian time. During this period, flyschoid or alluvial-deltaic complexes (Bol'shoi Karoi and Koksui formations) achieve their maximum development (Eganov and Sovetov, 1979; Sovetov, 1989). Coastal-marine or continental terrigenous sedimentation is sometimes interrupted by a supply of tuffogenic components (Kurgan Formation) (Korolev and Maksumova, 1964), or by a casual transgression of deeper-seated siliceous–dolomite facies (Chichkan Formation) (Ergaliev and Azerbaev, 1986). Fairly intensive tectonic movements and complicated, highly corrugated relief of both the paleobasin bed and adjacent areas, supplying great quantities of coarse terrigenous material, are typical for this stage.

The second transgressive–regressive stage of the Late Vendian–Early Cambrian involves the Berkuty dolomite formation as well as the Chulaktau phosphorite-bearing formation. This stage is a peculiar tectonic pause. In this period, the bottom relief irregularities that had appeared earlier are smoothed out by the growth of biohermal–stromatolite buildups, the paleobasin bottom is leveled, and conditions favorable for shoaly sedimentation are created, typical for lateral coastal plains of carbonate platforms. The complete reconstruction of sedimentation takes place. Instead of component precipitation onto the bottom and the determining effect of the near-bottom environment, the leading role is now played by biogenic–chemogenic processes related to the paleobasin level.

Finally, the third stage, encompassing the Middle Cambrian–Ordovician, corresponds to the existence of the carbonate platform. Following Wilson (1975), Cook *et al.* (1989, 1991) and Bazykin (1997) have clearly shown this. In this period, owing to the growth of bioherms, the substantially leveled paleoseafloor relief approached sea level in vast areas, and the biogenic–chemogenic carbonates were intensively accumulated in shallow waters. This process has a distinct cyclic character: each cycle starts from the accumulation of basal conglomerates formed at the expense of syngenetic breakup of laminites, continues with the formation of cross-bedded grainstones and marls, and concludes with the distribution of ribbon rocks, laminites and stromatolites (Bazykin, 1997). Certain sections, according to Bazykin, consist of up to 124 cycles corresponding to a rapid transgression of the marine basin and its subsequent slow regression. The total thickness of carbonate formation in the Cambrian–Ordovician of Lesser Karatau amounts to 2.6–3.3 km.

THE BIOGENIC RELIEF LEVELING AND FACIES OF THE VENDIAN–TOMMOTIAN PALEOBASIN

When the Berkuty–Chulaktau phosphorite-bearing deposits disconformably overlying terrigenous sequences are considered, one cannot help but notice the flattening-out of the seafloor relief which is clearly observed from the base of Berkuty (lower) dolomites to the ferromanganese stratum at the top of the phosphorite-bearing formation.

Indeed, the lower part of the dolomite sequence, often including basal layers (consisting of detritus, blocks, and fragments of layers of the underlying Karoi rocks) although sometimes devoid of them, is very sensitive to variations in the paleobasin bottom relief and smoothes out large irregularities. Fig. 1a shows that the thickness of this unit is increased in depressions and

decreased on uplifts. Such a behavior of the "lower" dolomites seems to be due to their reefogenic origin. Brodskaya and Kholodov (1965) and later Kholodov and Koryakina (1968), as well as Eganov and Sovetov (1979) have shown in their works that the bulk of dolomites consists of laminitic and stromatolitic bacterial-algal buildups (microbiolites).

The biogenic-reefogenic origin of lower dolomites is confirmed by the fact that laminitic structures are widely developed in them (Fig. 1b) and clearly registered in the sections of the Geres, Berkuty, and Karashat phosphorite ore occurrences, as well as in the Koksu and Kok Dzhon deposits. Besides, the roof of Berkuty dolomites in a number of cases presents a system of blocky salients (Fig. 1c and 1d), not infrequently separated by erosional depressions typical for bioherms. These depressions are sometimes filled with siliceous or siliceous-phosphate breccias containing large fragments of dolomites.

Outliers and blocks of dolomites up to 1.20–2.0 m long are often encountered not far from the roof of the Berkuty dolomites in the Berkuty, Dzhilan and Koksu sections (Fig. 1d). The figure shows that the overlying siliceous rocks, whose thickness decreases over the roof salients and dolomites outliers, substantially flattened out the bottom relief of the Chulaktau paleobasin.

All structural features of the lower dolomites, as well as their interrelations with the overlying siliceous-phosphate deposits, testify to the fact that they were formed within the surf zone of the marine paleobasin in the extremely shoaly environment.

The deposits with three different facial surroundings can be distinguished in the overlying siliceous sequences of Chulaktau. Seasonal-layered phthanites containing a substantial admixture of clay and organic matter are widely distributed in the most complete sections of the deep-water part of the phosphorite-bearing basin (the Koksu and Zhanatas deposits) (Kholodov, 1970a, 1970b). In their structure, composition, and bedding condition these rocks are close to the "V-bearing phthanites" of Greater Karatau. The deep-water silts of the Black Sea formed under conditions of sea water contamination by hydrogen sulfide can be considered as a recent analogue of these rocks.

The hydrosulfuric contamination of deep-water parts of the Tommotian paleobasin is proved, in our opinion, by great quantities of organic matter buried in its sediments and represented by antraxolite, graphite, and other catagenetic derivations of bitumoids. The characteristic presence of the remains of radiolaria, or more rarely, of sponge spicules (Ankinovich, 1961), possible findings of diatom shells (Gapeev, 1995; Ergaliev and Azerbaev, 1986), along with the complete absence of the remains of benthos communities, point to an anoxic environment during the burial of sediments. To a certain extent, this is also confirmed by the abundance of diagenetic sulfides (Kholodov and Paul', 1993).

The most reliable indicator of gas regime in the paleobasins waters is the stagnation coefficient, or the Mo/Mn ratio in the investigated sediments. As was shown in the previous work, it does not exceed several thousandths of parts in oxic basins, whereas in anoxic-hydrogen sulfide waters, it increases up to hundredth and tenth parts (Kholodov and Nedumov, 1991). According to the averaged data of S.G. Ankinovich and E.A. Ankinovich (1968), the Mo/Mn ratio varies from 0.08 to 0.09 for the primary phthanite deposits of Northwestern Karatau (Balasauskandyk) and Talas Alatau (Dzhebagly). The available data allow us to evaluate the stagnation coefficient for the primarily unaltered phthanites of Koksu (Lesser Karatau) as 0.07. Therefore, it is beyond doubt that seasonal-layered deposits in the deep parts of the Tommotian sea are planktonic sediments of hydrosulfuric geochemical facies.

The second facial type of siliceous deposits is represented by reefogenic sponge buildups and products of their hydrodynamic disintegration (spongolites) (Dzhumaliev and Kholodov, 1970; Kholodov, 1970a, 1970b).

Due to the poor preservation of primary siliceous structures and their frequent transformation into cryptocrystalline chalcedonolite, the regularities of their distribution have not been adequately studied. It is supposed that reefogenic sponge buildups were abundant in the Berkuty, Degeres, and Chulaktau districts. This is evidenced by the great thickness of siliceous sequences, the presence of blocky roof in them, as well as by the abundance of deep erosional depressions, not infrequently filled with pelletal phosphate material (Fig. 1e).

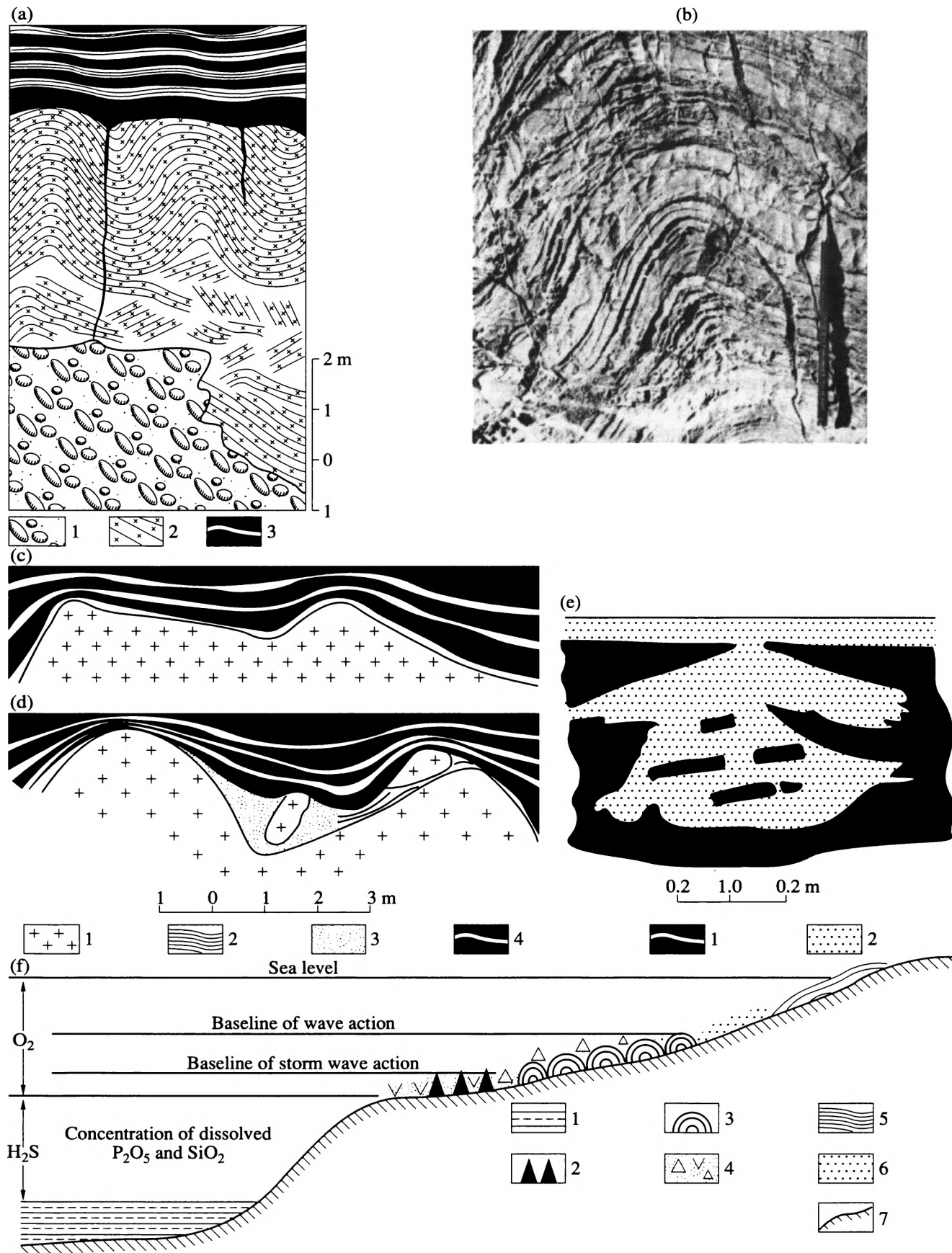
It should be emphasized that, unlike phthanites, the bulk of the sponge reef was evidently formed in tranquil shallow areas of the oxic zone.

Spongolites usually form interlayers, layers, lenses, as well as irregular aggregates filling erosional depressions. They are, as a rule, closely related to sponge reefs, but separate interlayers of them are also found among phthanites in the deeper parts of the paleobasin. It is not improbable that spongolites were formed at the expense of short-term lowerings of the wave activity baseline and disintegrations of sponge buildups.

Stromatolitic bioherms belong to the third facial type of siliceous formations. They were described in detail in the works of Eganov and Sovetov (1979), Eganov (1988), Litvinova (1990), and others.

Siliceous stromatolite buildups seem to be quite widely developed within the phosphorite-bearing basin. They were found at the Dzhilan, Karashat, Dzhetym Tal, T'esai, Berkuty, and Degeres ore occurrences. In all cases, these are the most coastal, littoral parts of the Tommotian paleobasin.

Due to the great geochemical mobility of silica during the secondary transformations of sedimentary rocks, which masks their primary structures, the forms of siliceous stromatolite buildups have been poorly studied. It is known that laminitic (thin-layered), disk-



shaped, dome-shaped, and columnar varieties, morphologically quite similar to stromatolites from the underlying Chichkan stratum, can be distinguished among them (Eganov, 1988; Litvinova, 1990).

It should be stressed that in the Karatau phosphorite-bearing basin, phthanites consisting only of silica are very rarely encountered. Most commonly, one encounters siliceous-phosphate biohermal formations in which bands made up by SiO_2 intricately alternate with those from phosphate material.

Another feature of siliceous-phosphate bioherms resides in the fact that they, like carbonate phytolites, frequently form siliceous-phosphate breccias confined inside the biogenic construction.

The phosphorite-bearing deposits themselves occupy a special place among the Chulaktau Formation deposits. Phosphoritic stromatolite buildups and pelletal phosphorites can be distinguished in them.

Aphanitic phosphate stromatolites were comprehensively described by Eganov (1988). The development of columnar, dome-shaped, stratiform, and numerous large spherical forms (oncolites, oncoïdes, etc.), usually localized within the phosphoritic layers and lenses, is established in the Tiesai, Dzhetym Tal, Dzhanan, and Aktas ore occurrences. Stromatolites are found in the most shallow, littoral part of the Tommotian sea, in the immediate vicinity of the coastline. In the deeper sections of Koksu and Zhanatas, they are represented by very rare laminitic stratiform formations.

Pelletal phosphorites consisting of multiple rounded phosphate particles, phosphate microfossils, and fragments of phosphate stromatolites, cemented by carbonaceous, phosphate, or siliceous cement, make up layers, lenses, and stratiform bodies. They are widely distributed within the relatively deep sections of the paleobasin in Koksu, Zhanatas, Kok Dzhan, Aksai, Chulaktau, and other deposits.

The comprehensive morphometric investigation of phosphorite pellets carried out in the last few years (Kholodov and Paul', 1993; 1995a, 1995b; 1996) allowed us to establish that these, as well as microfossils, are subject to two basic relationships. "The principle of matreshkas" implies that a limited number of typical forms of pellets are repeated many times as the particle size changes. "The principle of generations" finds its expression in multiple and periodic recurrence of the wide distribution of one-dimensional particles as their diameter grows.

Such morphometric features of phosphate pellets prove their biogenic origin and make it possible to state that they are components of stromatolites isolated from reefogenic buildups due to their substitution by phosphorus and the subsequent surf activity. From this viewpoint, stromatolitic phosphate bioherms serve as a starting material for forming the accumulations of phosphate pellets freely moving across the bottom.

Carbonate-phosphate rocks of the "ferromanganese stratum" represent a special type of deposits. They terminate the Chulaktau Formation section and may be considered to be a regressive homologue of the lower dolomites. Carbonate and bacterial and microbiolitic phosphate-carbonate laminites are abundant in the lower part of this member. Upward the section, they are replaced by nodular stromatolitic bioherms highly impregnated by iron sulfides in their unaltered part and by iron and manganese hydroxides in the weathering zone.

The carbonate-phosphate rock with the algal structure is located even higher. It contains a vast amount of large oncolites partially substituted by minerals of iron and manganese.

As a whole, all these deposits form a series of lenses from 0.2 to 0.5 km long and 3–4 m thick. It is obvious that during the "ferromanganese stratum" formation, the Tommotian seafloor relief was extremely smooth, and the basin underwent a regression and broke up into a number of very shallow-water microbasins (pools).

Thus, a quite intensive biogenic sedimentation was occurring within Lesser Karatau throughout the entire Berkuty–Chulaktau time. Indeed, owing to the reef-forming activity of cyanophyceae and cyanobacteria, creating stromatolite buildups, the relief was gradually flattened, and the conditions for the carbonate platform formation were prepared.

Variations in the mineral composition of reefogenic buildups in the section of Berkuty–Chulaktau deposits can be understood only if the general facial and geochemical situation within the Vendian–Cambrian paleobasin of Bol'shoi and Lesser Karatau is considered (Fig. 1f).

After the thick sequence of Baikunur tillite-type conglomerates had been deposited, the regime of the deep-water marine basin with the gravitational stratification and hydrogen sulfide contamination of waters was established in the part of the paleobasin that was located in the northwest of the Greater Karatau Range and in the Talas Alatau region.

Laminated carbonaceous siliceous-clayey-carbonate phthanites had accumulated here throughout the whole

Fig. 1. Formation of bacterial-algal buildups and leveling of the Tommotian paleobasin bottom. (a) Structure of the "lower" dolomite member within the Geres ore occurrence: (1) alluvial conglomerates, (2) dolomites, and (3) cherts; (b) stromatolitic structure of "lower" dolomites in the Geres district; (c, d) relationship between "lower" dolomites and overlying siliceous deposits in the Dzhanan district: (1) dolomite, (2) phosphate-siliceous laminite, (3) phosphate-siliceous bioclastite, and (4) cherts; (e) erosional depression in siliceous deposits of the Berkuty district: (1) cherts and (2) pelletal phosphorite; (f) facial scheme of the Tommotian paleobasin in Karatau: (1) laminated alternation of carboniferous phthanites, clayey, and carbonate bands in Greater Karatau, (2) "sponge" reefs, (3) carbonate bioherms and biostromes, (4) spongolites, (5) bacterial-algal mats, (6) bioclastites from bacterial-algal mats, and (7) bottom contours.

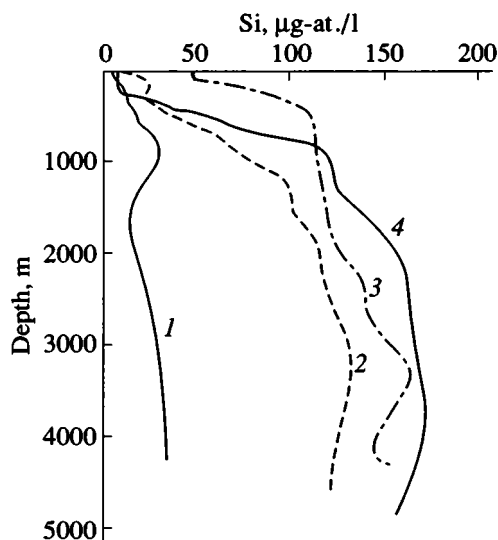


Fig. 2. Silicon distribution in oceanic waters (Bogoyavlenskii, 1966). (1) Atlantic Ocean; (2) Indian Ocean; (3) Antarctic waters; (4) Pacific Ocean.

Tomotion age. Their basic component was a planktonogenic siliceous, carbonate, and organic substance, which occasionally descended onto the paleobasin bottom as a flux of the remains of radiolaria, diatoms, and other organisms, reflecting the seasonal bloom of plankton. Clay material supplied from the land was diluted with planktonogenic components of silts, and the whole sequence acquired a characteristic rhythmical-layered structure.

Along with the basic rock-forming component, rhythmical-layered phthanites contain increased amounts of U, V, P, Cr, Mo, Re, Pb, Ba, and Sr (Ankinovich and Ankinovich 1968; Kholodov, 1973). Many of these elements were intensively supplied from the land. Thus, it was shown in (Ankinovich and Ankinovich, 1968) that the average content of P_2O_5 in unaltered siliceous rocks (phthanites or lyddites) can be evaluated as 0.71%. If it is considered that the average content of P_2O_5 in the sedimentary shell is 0.145%, it becomes obvious that the intensity of phosphorus accumulation in the Tomotion phthanites exceeded that in other sedimentary formations by a factor of 4.5–5.

The quantity of P_2O_5 distributed in the Holocene and recent silts of the Black Sea also considerably exceed the above values of concentration. According to Volkov and Sevast'yanov (1968), the average P_2O_5 content here varies from 0.18 to 0.20% (Kholodov and Paul', 1995b).

It is interesting that the phosphorus concentration in the Tomotion phthanites of Karatau is excessive in comparison with that of organic matter buried in them. Indeed, the organic carbon content in phthanites sometimes reaches 10–15% but on the average, it is 1.34% in Dzhebagly and 1.80% in Balasauskandyk. Since, according to the data of Redfield (1958), saproplanktonogenic organic matter is characterized by the ratio $P/C_{org} = 1/42$, it is easy to estimate that during precipi-

tation of these quantities of organic carbon in the form of planktonogenic suspension, only 0.07–0.09% of P_2O_5 can be contributed into the sediment. It constitutes approximately one-tenth of the phosphorus pentoxide distributed in phthanite sequences.

Even if we suppose that dia- and catagenetic losses in the Cambrian sequences amounted to 60–70%, we would have to assume that a certain part of phosphorus was not connected with the biogenic circulation of the Tomotion sea, but was supplied from the land.

This statement corresponds well to the concepts of the Vendian–Cambrian epoch of pancontinental phosphorite formation (Kholodov, 1970a, 1970b, 1973), the evolution of provenances in the Riphean and Phanerozoic (Kholodov, 1975), and the supply of substantial phosphorus masses into terminal basins at the expense of the disintegration of massifs of ultrabasic and alkaline magmatic rocks that are predominant on the continents (Kholodov, 1995).

Intensive processes of microbiological sulfate reduction caused the partial decomposition of organic matter, which is supplied into deep-water silts of the Tomotion sea, and vigorous sulfide formation. The residual H_2S and CO_2 entered into the suprabottom water, where, under conditions of decelerated water circulation, a great hydrogen sulfide and carbonate reservoir was being formed. Similar to the present-day Black Sea (Kholodov and Paul', 1995b), the waters of hydrogen sulfide zone in the Tomotion time contained considerable quantities of dissolved P and Si.

In the previous works, following Bruevich (1953), Fonselius (1974), Baturin (1978), and other investigators, we have shown that, at the average phosphorus concentration in marine and oceanic waters 70 µg/l, this element is accumulated in the waters of hydrogen sulfide zones up to 230 and even 300 µg/l (Kholodov and Paul', 1995a, 1995b).

Silicon seems to also behave similarly. The average concentration of Si dissolved in the World Ocean waters is evaluated to be 2.07 mg/l (Ivanenkov, 1979).

The distributional regularities for Si dissolved in oceanic and marine waters are very similar to those for P. In the photosynthesis zone, where Si is absorbed by plankton, its content is minimum but it grows noticeably toward the bottom of basins (Fig. 2). In the open ocean, the surface waters contain 0.05–0.20 mg/l of Si, whereas in the deep waters, its content increases 20–70 fold. Approximately the same Si content is found in the silt waters of pelagic parts of the ocean, where sulfate reduction processes come to a standstill due to the deficiency of organic matter (Shishkina, 1979).

A different picture is observed in the silts of coastal zones, strong enriched in organic matter. Shishkina (1979), Ivanenkov (1979), *et al.*, have shown that the Si content there reaches 30 mg/l and exceeds its content in the near-bottom waters by a factor of 30. Here, Si can readily diffuse from silts into the suprabottom water and thereby create secondary accumulations of SiO_2 in water.

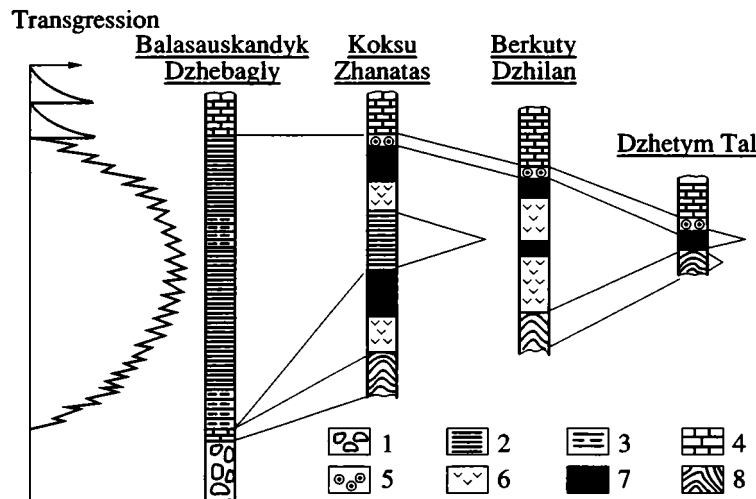


Fig. 3. Transgressive-regressive structure of the Chulaktau Formation within the Greater and Lesser Karatau Ranges. (1) Tillite-type deposits of the Baikunur formation; (2) laminated carboniferous-siliceous-clayey-carbonate rocks of the Kurumsak and Kulantau formations; (3) laminated and coarse-layered cherts; (4) deposits of the Cambrian-Ordovician carbonate platform; (5) biostromal-oncolithic ferromanganese formations; (6) interval of sections where siliceous deposits prevail; (7) interval of sections where layers of pelletal phosphorites prevail; (8) carbonate bioherms of "lower" dolomites.

According to the data of Bruevich (1953) and Skopintsev (1975), the Si concentration in the euphotic zone of the Black Sea is 0.8–1.5 mg/l. However, in the deep zones, it increases up to 7–9 mg/l which is 3–5 times higher than in the oceanic deep waters.

It is obvious that, owing to the development of hydrogen sulfide contamination, both dissolved P and Si are intensively concentrating in the present-day Black Sea waters. It can be supposed that the similar diagenetic mechanism ensuring high contents of these elements in the suprabottom water was also at work in the hydrogen sulfide reservoir of the Tommotian sea (Fig. 1f).

The redox boundary in the Vendian-Cambrian paleobasin of Karatau evidently did not remain constant. Sometimes it lowered towards the continental slope plunge, and at other times it captured the shelf's seaward sectors. Above this interface, in the zone of dissolved oxygen predominance, diverse biogenic and biogenic-algal buildups were widely distributed within the phosphorite-bearing basin of Lesser Karatau. At the very margin of the shelf, in its most submerged part, in areas free from the suspension supply and constant wave activity, the colonies of siliceous sponges extracting Si from seawater during their lifetime were forming. During sea shoaling they became a source for forming interlayers and lenses of spongolites.

Near the shore, within the subtidal zone, vast areas of the shelf were occupied by carbonate stromatolitic bioherms and biostromes. It cannot be doubted that in the Berkuty time when bioherms prevailed, as well as during the ferromanganese stratum formation, when biostromes and oncolite aggregates prevailed, the life-long carbonization of cyanophyceal and cyanobacteria colonies proceeded elsewhere. Carbonates were concentrated at the expense of both physiological and bio-

chemical processes (Krylov, 1975; Maslov, 1961, Serebryakov, 1975). It is also obvious that carbonatized bands of laminites primarily alternated with hyaline bands.¹ The total carbonatization of layers and buildups was completed in the process of postsedimentary transformations.

Towards the intertidal and supratidal zones, the dimensions of biogenic buildups gradually decreased. The hyaline formations began to play an ever-increasing role in the alternation of bacterial-algal bands, and therefore, the facies of bioherms and biostromes gradually transformed into the facies of hyaline bacterial-algal mats and laminites dominating in the tidal zone.

TRANSGRESSIVE-REGRESSIVE MOVEMENTS OF THE SEA AND THE MECHANISM OF PHOSPHORITE FORMATION

The basic geological process that has determined the signature of the phosphorite-bearing formation consisted of transgressive-regressive events in the history of marine paleobasin which were clearly reflected in the structure of the Lesser Karatau sections (Fig. 3).

According to the conceptions of Maksumova (1973), Korolev and Maksumova (1976), Missar-zhevskii and Mambetov (1981), and other investigators, at the end of development of the Kurgan Formation the continental regime was established throughout the territory of Lesser Karatau and Talas Alatau, the relief had been leveled, and a fairly thick weathering crust had begun to form. This epoch of tectonic process stabilization was

¹ Following Monty (1965) and Krylov (1975) we shall refer to bacterial-algal layers enriched in organic matter as "hyaline layers of stromatolites."

interrupted by the development of downward movements and by the transgression of marine basins.

The coastal-deltaic red-colored deposits of the Kyr Shabakty Formation formed during the first stage of transgression were gradually replaced by coastal-marine dolomites.

The Berkuty dolomites, on one hand, may seem to terminate the Kyr Shabakty stage of development, but, on the other hand, they are separated from the deposits of this cycle due to the washout and sharply transgressive overlying on the sequences of variable age.

Undoubtedly, the lower dolomite sequence opens a marine transgression which gradually covered almost the whole area of the phosphorite-bearing basin (Fig. 3).

If we take into account that the lower dolomites vary from 40–15 m to 0.5 m in thickness and may even completely wedge out (Kholodov and Koryakin, 1968), that all dolomites display the signs of stromatolitic bioherms, and that the thickness of overlying phosphorite-bearing deposits is also reduced to the minimum in the areas of dolomite wedge out, then doubts concerning their synchronism in all places will arise. Moreover, it can be supposed that here, we are dealing with a certain carbonate–stromatolite–biohermal facies that reflects the paleobasin shift deep into the continent.

In this connection, it is interesting to recall the past controversies about the age of Berkuty dolomites. In fact, certain investigators related them to the Vendian, and the boundary between the Precambrian and Cambrian was drawn across the top of dolomites (B.M. Keller, V.G. Korolev, I.N. Krylov, V.V. Missarzhevskii, A.M. Mambetov, etc.). Others related the dolomites to the Lower Cambrian (V.N. Kholodov, E.A. Eganov, Yu.K. Sovetov, G.Kh. Ergaliev, N.V. Pokrovskaya, etc.).

We think that the viewpoint of Missarzhevskii and Mambetov (1981), as well as the hypothesis of Ergaliev and Pokrovskaya (1977) are both valid. According to the latter, the Berkuty dolomites are consecutive, their most ancient facies being associated with the deepest and thickest sections of the Chulaktau Formation (Koksu, Zhana-tas), while the youngest ones are located in the shallow-water part of the paleobasin among the sections with sharply reduced thicknesses (Dzilan, Dzhetyr Tal).

The transgression of Tommotian sea in Lesser Karatau was maximum after deposition of the lower strata of cherts and phosphorites, when the facies of laminated phthanites and shales—the typical sediments of a hydrogen sulfide-bearing paleobasin,—appeared and widely spread in the Geres–Koksu Depression (Fig. 3). During this period, cherts and pelletal phosphorites were intensely deposited within the entire intertidal zone.

The transgression of hydrogen sulfide-bearing paleobasin into the shallow coastal zone could not have passed without leaving a trace for the hydrogen sulfide reservoir itself. It is common knowledge that at the upper boundary of a hydrogen sulfide zone the physicochemical equilibrium is maintained at the expense of

the biochemical and chemical oxidation of H_2S and its transformation into dissolved sulfates (Kholodov and Paul', 1995; Sorokin, 1982; Volkov, 1960; Volkov and Sevastianov, 1968). It is evident that this process should have become extremely intensified in the shallow-water zone, where the vigorous surf activity permanently promotes the extensive dissolution of oxygen in seawater. The processes of H_2S oxidation in the shallow-water zone should also have been favored by the metabolic activity of bacterial–algal colonies intensely consuming CO_2 and releasing oxygen (Cloud, 1968).

Another process aimed at the extraction of dissolved hydrogen sulfide from seawater on the Tommotian sea shoals was intensified sulfide formation. Here, we should recall that the leading role in this process belongs to widely distributed iron, whose stratospheric clarkite is evaluated as 3.33%. Iron hydroxide, which was widespread in the red-colored rocks of the Kyr Shabakty Formation, predominated in all deposits of the continental terrigenous stage of the Lesser Karatau development; probably, it was intensely supplied from the shore into the marine basin.

Reduction of Fe^{+3} to Fe^{+2} and its bonding into pyrite removed from solution vast quantities of hydrogen sulfide. The reality of this process is confirmed by the great amount of pyrite encountered in unaltered dolomites, phosphorites and cherts.

The loss of dissolved hydrogen sulfide during the marine basin transgression toward the shallow-water shelf caused a whole chain of geochemical processes. First of all, the transition of hydrogen sulfide solutions into oxic ones was accompanied by the precipitation of Si, P and Mn. Let us remember that one liter of hydrogen sulfide-bearing water (e.g., the Black Sea water) contains about 9010 μg of Si, 300 μg of P, and up to 300 μg of Mn, whereas their average concentrations in oxic seawater are evaluated as 2070, 70, and 2 $\mu g/l$, respectively.

This means that during gas composition transformations, approximately 7000 μg (7 mg) of Si and 230 μg of P can be liberated from each liter of seawater. One may think that the evolving components readily substituted stromatolite buildups which primarily had the carbonate–hyaline composition.

Multiple observations of structural relationships of rocks belonging to the Chulaktau Formation (Fig. 4) testify to the fact that the processes of substitution of biogenic–algal formations by silica and phosphorus played an essential role in forming siliceous rocks and phosphorites.

Sketches 4a, 4b, and 4c characterize the relationships observed between the lower dolomites and the overlying cherts. Frequently, within the Berkuty and Geres ore occurrences, the upper parts of dolomite stromatolite buildups are substituted, and the relics of dolomite bodies possessing unique configurations turned out to be enclosed within cherts. Concretions and vertical veins filled with SiO_2 can be found in places in the dolomites. These veins penetrate deeply into carbonate

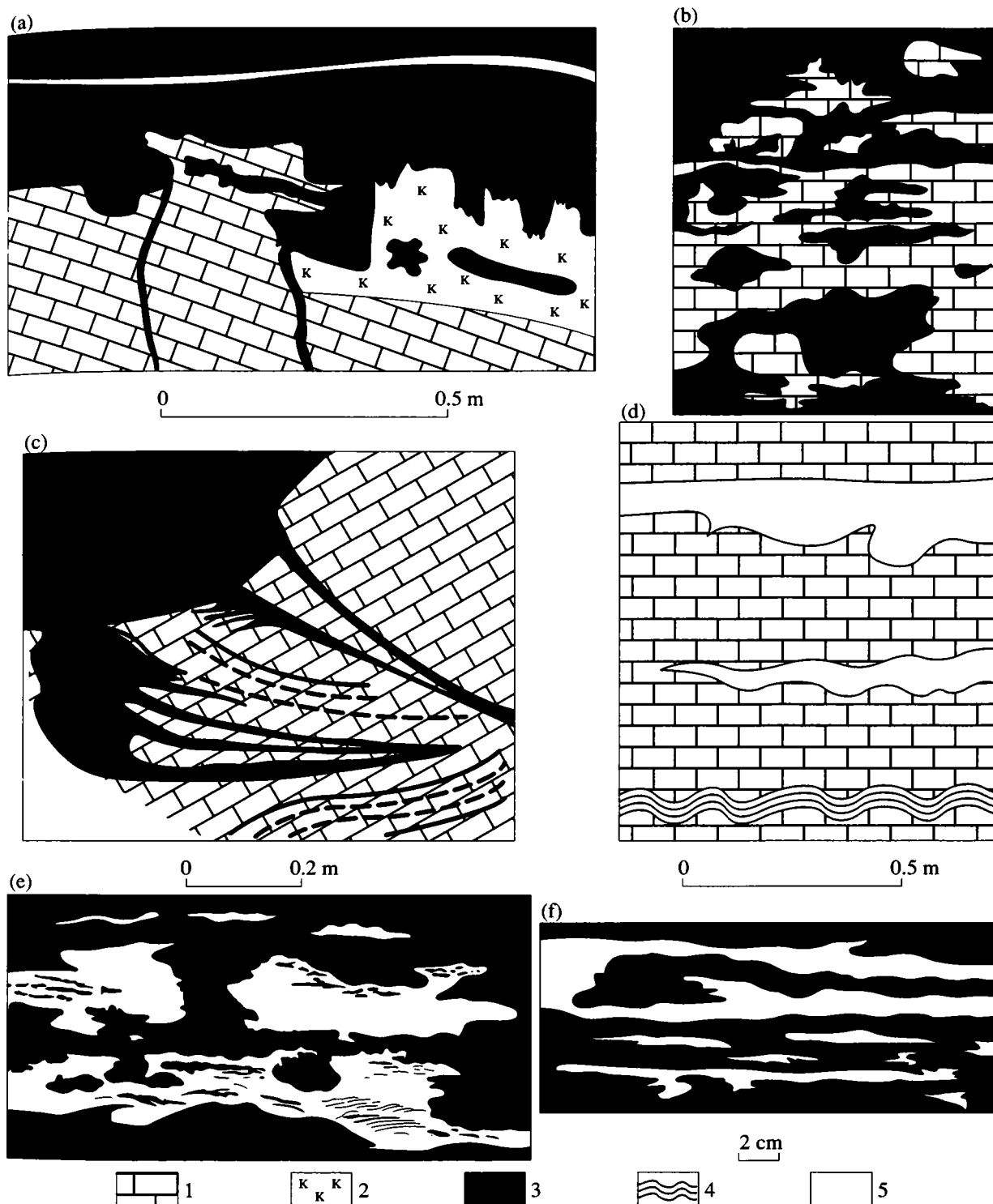


Fig. 4. Structural interrelations of "lower" dolomites, cherts, and phosphorites in sections of the Chulaktau Formation in Lesser Karatau. (a) Contact of "lower" dolomites and cherts within the Berkuty ore occurrence; (b) interrelations of dolomites and cherts in the Geres district (Eganov and Sovetov, 1979); (c) silicification of the roof of "lower" dolomites in the Dzhilan district; (d) phosphatization and manganization of dolomites in the Kyr Shabakty mountain area; (e and f) silicification of phosphate layers in the Aksai deposit (Eganov and Sovetov, 1979). (1) Dolomite; (2) coarse-crystalline calcite; (3) cherts; (4) manganification of laminites; (5) phosphorite.

layers. Quite often, they are encountered in the Dzhanal ore occurrence and Chulaktau deposit.

It is interesting that phosphorites are so aggressive with respect to the lower dolomites. In the Kyr Shabakty ore occurrence, frequently lenticular-patchy inclusions of aphanitic phosphorites, seemingly substituting carbonates, are localized inside the dolomite bodies.

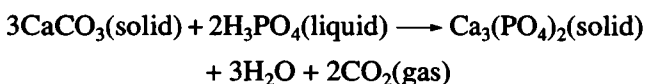
The characteristic interrelation between cherts and phosphorites was described in the monograph of Eganov and Sovetov (1979). In the siliceous member of the Aksai and Zhanatas deposits, as well as the Akdzhar and Berkuty ore occurrences, cherts replace pelletal phosphorites that are preserved in the outcrops in the form of "islets," sophisticated lenses, or relic inclusions (Fig. 4e, 4f).

It may be supposed that at least a certain part of these interpenetrations occurred during the sedimentation of P_2O_5 and SiO_2 from hydrogen sulfide solutions injected into the shallow-water zone.

It is noteworthy that Mn was also accumulated in some places in the lower dolomites. The strong manganification of rocks of this stratum, which is sometimes associated with the washout surfaces, is registered within the Chulaktau deposit as well as the Kyr Shabakty and Tamdy ore occurrences.

The substitution of carbonate stromatolite buildups by silica is mainly due to the fact that, all other conditions being equal, the acidic medium is much more favorable for SiO_2 precipitation than the alkaline one. On the contrary, the slightly alkaline medium is the most favorable for the carbonate sedimentation. In other words, carbonates and silicites usually act as physicochemical antipodes, which results in their complicated spatiotemporal interrelations in nature (Peterson and Von der Borch, 1963; etc.; Teodorovich, 1950).

It should be also noted that among carbonic, silicic, and phosphoric acids the latter is the strongest. In this connection, the chemical reaction



under the normal thermodynamic conditions will always be shifted to the right side, towards the phosphate formation (Nekrasov, 1973). This circumstance predetermines the possibility for substitution of stromatolite formations by phosphate minerals.

The chaotic spatial interrelations among stromatolitic dolomites, cherts, and aphanitic phosphorites within the Chulaktau sequence, illustrated in Fig. 4, might seem to exclude the possibility of detailed comparison between different members in the basin area and to prevent clear-cut stratification of the sequence.

However, this is not the case. The point is that pelletal phosphorites and spongolite accumulations usually make up layers or lenticular-layered formations clearly restricted by the roof and the base and traced to great distances. As shown in Fig. 3, in both halves of a transgressive-regressive cycle the layers of pelletal phos-

phorites concentrate in the upper part. They terminate both transgression and regression.

Such a bedding of pelletal phosphorites is undoubtedly connected with their origin. Indeed, we think that the pellets represent a peculiar component or fragments of bacterial-algal buildups, which are completely substituted by phosphate minerals during their lifetime (Kholodov and Paul', 1995a, 1995b). Many of them are similar in shape to terrestrial plant spores.

It is possible that the noted resemblance is not accidental. Recently, more and more evidence has appeared proving the fact that higher algae, which possessed ribbon-shaped layers and complicated reproductive organs (sporangia), are encountered in nonmineralized bacterial-algal communities of the Vendian and Lower Paleozoic (Ishchenko, 1984, etc.).

In all instances, the substitution of hyaline parts of bacterial-algal buildups by P, unlike their substitution by silica and carbonates, facilitated the preservation of the finest details of their structure and, in the final analysis, favored their separation from the bulk of stromatolite buildup. Due to the exceptional strength of phosphoric acid, the substitution was accompanied by disintegration of the bacterial-algal community into separate fragments (components) which were buried and reburied in this very place.

A considerable time interval was required for the accumulation of great masses of such bioclastic phosphate layers and lenses, and for this reason, they always terminate transgression and regression phases.

And, finally, the final stage of the Chulaktau epoch is formation of the regressive ferromanganese stratum. Similarly to the lower dolomites, the deposits of the ferromanganese stratum are consecutive; the most ancient carbonate-phosphate laminites and oncolites were formed in drying-up pools of Dzhetym Tal and Karashtat, while the youngest ones—in a separate section of the Koksu and Zhanatas deposits (Fig. 3).

In conclusion, it should be stressed that all compositional and structural features of the Chulaktau phosphorite-bearing formation can be unequivocally explained when represented as a biogenic leveling stage of the marine paleobasin relief, connected, on the one hand, with the carbonate platform formation, and on the other hand, with the results of transgressive-regressive movements of the hydrosulfuric marine paleobasin that "reworked" its bacterial-algal buildups developed in shallow-water oxic environments.

CONCLUSION

In light of the proposed model, an explanation can be found many features of ancient pelletal phosphorite deposits. Thus, for example, the close relation existing between the distribution of phosphorite and carbonate rocks, already noted in the works of Kazakov *et al.* (1957) and Shatskii *et al.* (1955), etc., becomes understandable. It manifests itself in connection with the fact

that phosphorite formation can be considered as a certain stage in the carbonate platform development, i.e., a certain period in its formation.

Paragenetic associations of ancient phosphorites with black, rich in organic matter, "metal-bearing" shales and phthanites, cherts and ferromanganese ores investigated in the works of Al'tgauzen (1956), Ankinovich (1961), Bushinskii (1966), Kholodov (1970a, 1970b; 1973), etc., can be interpreted as different facies of the hydrogen sulfide-bearing marine paleobasin.

And, finally, the link of phosphorites to transgressions widely discussed in many previous works (Arkhangel'skii, 1927; Bushinskii, 1952; 1966; Gimmel'farb, 1959) acquires a new and somewhat unusual interpretation: phosphorites represent a transgressive facies of a hydrosulfuric paleobasin that deposited the excessive quantities of accumulated in solution chemical materials (in the first place, SiO_2 , P_2O_5 , and MnO) in the areas of intensive bacterial-algal activity.

In this connection, it should be noted that the similarity in the structure of phosphorite-bearing sequences in Karatau, Georgine, Rocky Mountains, Lake Khubsugul, and Chinese Platform, noticed by Eganov and Sovetov (1979), evidently allows the extrapolation of our model to other phosphorite-bearing basins of the world.

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REFERENCES

- Al'tgauzen, M.N., *Prichiny vozniknoveniya epokhi nako-pleniya redkikh metallov i fosfora v morskikh osadkakh nizhnego paleozoya* (Reasons for the Beginning of the Accumulation Epoch of Rare Metals and Phosphorus in Marine Sediments of the Lower Paleozoic), Moscow: Gosgeoltekhizdat, 1956.
- Ankinovich, S.G., *Nizhnii paleozoi vanadienosnogo basseina Severnogo Tyan'-Shanya i zapadnoi okrainy Tsentral'nogo Kazakhstana* (The Lower Paleozoic in the Vanadium-bearing Basin of the Northern Tien Shan and Western Margin of Central Kazakhstan), Alma-Ata: Akad. Nauk KazSSR, 1961.
- Ankinovich, S.G. and Ankinovich, E.A., The Conditions of Accumulation and Formation of Ore-bearing Shales of the Lower Paleozoic in Southern Kazakhstan, in *Geokhimiya osadochnykh porod i rud* (Geochemistry of Sedimentary Rocks and Ores), Moscow: Nauka, 1968, pp. 356-375.
- Arkhangel'skii, A.D., Stratigraphy and Geological Conditions of the Formation of Russian Phosphorites, in *Fosfority SSSR* (Phosphorites in the USSR), Leningrad: Geolkom, 1927, pp. 13-23.
- Baturin, G.N., *Fosfority na dne okeana* (Phosphorites at the Oceanic Bottom), Moscow: Nauka, 1978.
- Bazykin, D.A., Shallowing-Upward Cycles in the Lower Paleozoic Shallow-Marine Carbonates of Malyi Karatau, Kazakhstan, *Litol. Polezn. Iskop.*, 1997, no. 2, pp. 115-132 [*Lithol. Miner. Resour.*, vol. 32, no. 2, pp. 97-112].
- Bogoyavlenskii, A.P., Distribution and Migration of Dissolved Silicic Acid in Oceans, in *Geokhimiya kremezemov* (Geochemistry of Si), Moscow: Nauka, 1966, pp. 11-37.
- Brodskaya, N.G. and Kholodov, V.N., The Possibility of Reefogenic Origin of Dolomites in the Phosphorite-bearing Sequence of Lesser Karatau, *Dokl. Akad. Nauk SSSR*, 1965, vol. 165, no. 6, pp. 1365-1368.
- Bruevich, S.V., Chemistry and Biological Productivity of the Black Sea, *Trudy Inst. Okeanol. Acad. Nauk Ross.*, 1953, vol. 7, pp. 12-56.
- Bushinskii, G.I., *Apatit, fosforit, vivianit* (Apatite, Phosphorite, and Vivianite), Moscow: Akad. Nauk SSSR, 1952.
- Bushinskii, G.I., *Drevnie fosfority Azii i ikh genezis* (Ancient Phosphorites of Asia and Their Genesis), Moscow: Nauka, 1966.
- Cloud, P.E., Pre-Metazoan Evolution and the Origin of the Metazoa, in *Evolution and Environment*, New York: Yale Univ. Press, 1963.
- Cook, H.E., Taylor, M.E., Zhemchuzhnikov, S.V., et al., Evolution of Early Paleozoic Carbonate Seamount, Malyi Karatau Range, Southern Kazakhstan, USSR. New Evidence for Early History of Kazakhstan, *28th Int. Geological Congr. in Washington, D.C. Am. Geophys. Union*, 1989, pp. 322-323.
- Cook, H.E., Taylor, M.E., Zhemchuzhnikov, S.V., et al., Comparison of Two Early Paleozoic Carbonate Submarine Fans-Western United States and Southern Kazakhstan, Soviet Union, *Paleogeography of Western United States. Pacific Section SEPM*, 1991, vol. 67, pp. 847-872.
- Dzhumaliev, T.D. and Kholodov, V.N., Siliceous Rocks of the Phosphorite-bearing Chulaktau Formation in Lesser Karatau and Their Formation Conditions, *Dokl. Akad. Nauk SSSR*, 1970, vol. 194, no. 2, pp. 414-417.
- Eganov, E.A., *Fosforitoobrazovanie i stromatolity* (Phosphorite Formation and Stromatolites), Novosibirsk: Nauka, 1988.
- Eganov, E.A. and Sovetov, Yu.K., *Karatau-model' regiona fosforitonakopleniya* (Karatau—the Model of a Phosphorite Accumulation Region), Novosibirsk: Nauka, 1979.
- Ergaliev, G.Kh. and Pokrovskaya, N.V., *Nizhnnekembriiskie trilobity Malogo Karatau (Yuzhnyi Kazakhstan)* (The Lower Cambrian Trilobites of Lesser Karatau, South Kazakhstan), Alma-Ata: Nauka, 1977.
- Ergaliev, G.Kh. and Azerbaev, N.A., The Cambrian System. Greater Karatau, in *Geologiya i metallogeniya* (Geology and Metallogeny of Karatau), Alma-Ata: Nauka, 1986.
- Fonselius, S.H., Phosphorus in Black Sea, in *Black Sea—Geology, Chemistry, Biology*, Tulsa: Okla, 1974, pp. 144-151.
- Gapeev, A.P., Cambrian Forms of Diatoms in the Lesser Karatau Deposits, *Litol. Polezn. Iskop.*, 1995, no. 3, pp. 236-252 [*Lithol. Miner. Resour.*, vol. 30, no. 3, pp. 209-223].
- Gimmel'farb, B.M., The Basic Geological Regularities in the Distribution of Phosphorite Deposits in the USSR, in *Geologiya mestorozhdenii gorno-khimicheskogo syr'ya* (Geology of Deposits of Mining and Chemical Raw Materials), Moscow: Khimizdat, 1959, pp. 7-79.
- Ishchenko, A.A., The Paleoeological Aspect of the Problem Concerning the Origin of Higher Plants, Abstracts of Papers, *27th Session MGK*, Moscow: Nauka, 1984, vol. 9, part 2, pp. 51-52.

- Ivanenkov, V.N., General Information on Nitrogen, Phosphorus, and Silicon, in *Khimiya okeana. Khimiya vod okeana* (Chemistry of the Ocean: Chemistry of Oceanic Waters), Moscow: Nauka, 1979, vol. 1, pp. 176–184.
- Kazakov, A.V., Tikhomirova, M.M., Plotnikova, V.I., et al. *Mineralogicheskie i fiziko-khimicheskie issledovaniya nekotorykh osadochnykh porod i poleznykh iskopaemykh* (Mineralogical and Physicochemical Investigations of Some Sedimentary Rocks and Minerals), Moscow: Akad. Nauk, 1957.
- Kholodov, V.N., On Vanadium-Bearing Phthanites in the Chulaktau Formation of Lesser Karatau, *Dokl. Akad. Nauk SSSR*, 1970a, vol. 193, no. 6, pp. 1384–1387.
- Kholodov, V.N., On Metallogeny of the Vendian and Cambrian in Eurasia: Communication 1. Pre-Vendian Uplifts as a Possible Source of Ore Components, *Litol. Polezn. Iskop.*, 1970b, no. 2, pp. 130–147.
- Kholodov, V.N., Metallogeny of the Vendian and Cambrian in Eurasia: Communication 2. Sedimentary Ores of Vanadium, Phosphorus, Iron, and Manganese and Conditions of Their Formation, *Litol. Polezn. Iskop.*, 1970c, no. 4, pp. 29–44.
- Kholodov, V.N., *Osadochnyi rudogenez i metallogeniya vanadiya* (Sedimentary Ore Genesis and Metallogeny of Vanadium), Moscow: Nauka, 1973.
- Kholodov, V.N., The Compositional Evolution of Provenances During the Earth's History, in *Problemy litologii i geokhimiya osadochnykh porod i rud* (The Problems of Lithology and Geochemistry of Sedimentary Rocks and Ores), Moscow: Nauka, 1975, pp. 191–209.
- Kholodov, V.N., The Phosphorite Forming Epochs as a Reflection of Magnetism Evolution in the Earth's History, *Dokl. Akad. Nauk SSSR*, 1995, vol. 247, no. 4, pp. 237–240.
- Kholodov, V.N. and Koryakin, A.S., The Paleogeography of Lesser Karatau (Kazakhstan) during the Age of "Lower" Dolomites Deposition in the Phosphorite-Bearing Sequence, *Byull. Mosk. O-va Ispyt. Prir., Otd. Geol.*, 1968, vol. 43 (6), pp. 70–84.
- Kholodov, V.N. and Nedumov, R.I., The Geochemical Criteria for Hydrogen Sulfide Contamination of Ancient Water Basins, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1991, no. 12, pp. 74–82.
- Kholodov, V.N. and Paul', R.K., The Problem of Ancient Phosphorites Genesis, *Litol. Polezn. Iskop.*, 1993, no. 3, pp. 110–126.
- Kholodov, V.N. and Paul', R.K., Phosphate Pellets of the Karatau Phosphorites as an Indicator of Their Genesis, *Litol. Polezn. Iskop.*, 1995a, no. 1, pp. 61–75.
- Kholodov, V.N. and Paul', R.K., The Black Sea as a Geochemical Model of Phosphate Accumulation, *Litol. Polezn. Iskop.*, 1995b, no. 6, pp. 563–581.
- Kholodov, V.N. and Paul', R.K., The Problem of Pellet Origin in the Cambrian Deposits of Karatau, *Dokl. Ross. Akad. Nauk*, 1996, vol. 346, no. 4, pp. 514–517.
- Korolev, V.G. and Maksumova, R.A., The Late Precambrian of Talas Alatau, *Preprint of the Frunze Polytechn. Inst., Geol. Mining*, Frunze, 1964, issue 19, pp. 48–55.
- Korolev, V.G. and Maksumova, R.A., The Kyr Shabakty Formation and the Relationship between the Karoi and Tamdy Groups of the Lesser Karatau Range, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1976, no. 7, pp. 84–89.
- Krylov, I.N., *Stromatolity rifeya i fanerozoia SSSR* (Stromatolites of the Riphean and Phanerozoic in the USSR), Moscow: Nauka, 1975.
- Litvinova, T.B., On the Stromatolithic Origin of the Siliceous Stratum in the Chulaktau Formation of Lesser Karatau, *Litol. Polezn. Iskop.*, 1990, no. 2, pp. 88–97.
- Maslov, V.P., Algae and Carbonate Sedimentation, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1961, no. 12, pp. 68–92.
- Maksumova, R.A., The Vendian Weathering Crusts in the Karatau Range, Southern Kazakhstan, *Litol. Polezn. Iskop.*, 1973, no. 4, pp. 133–138.
- Missarzhevskii, V.V. and Mambetov, A.M., *Stratigrafiya i fauna pogranichnykh sloev kembriya i dokembriya Malogo Karatau* (Stratigraphy and Fauna of the Cambrian and Precambrian Boundary Layers in Lesser Karatau), Moscow: Nauka, 1981.
- Monty, C., Recent Algal Stromatolites in the Windward Lagoon, Andros Island, Bahamas, *Ann. Soc. Geol. Belgique*, 1965, vol. 88, nos. 5–6, pp. 68–75.
- Nekrasov, B.V., *Kurs obshchei khimii* (The Course of General Chemistry), Moscow: Khimiya, 1973.
- Peterson, M.N. and Von der Borch, C.C., Chert: Modern Inorganic Deposition in a Carbonate-precipitating Locality, *Science*, 1963, vol. 149, pp. 1501–1503.
- Redfield, A.G., The Biological Control of Chemical Factors in the Environment, *Am. Sci.*, 1958, vol. 46, pp. 205–211.
- Shatskii, N.S., Phosphorite-bearing Formations and Classification of Phosphorite Deposits, in *Soveshchanie po osadochnym porodam* (Meeting on Sedimentary Rocks), Moscow: Akad. Nauk SSSR, 1955, pp. 7–99.
- Shishkina, O.V., Mud Waters, in *Khimiya okeana. Geokhimiya donnykh osadkov* (Chemistry of the Ocean: Geochemistry of Bottom Sediments), Moscow: Nauka, 1979, vol. 2, pp. 252–270.
- Serebryakov, S.N., *Osobennosti formirovaniya i razmeshcheniya rifeiskikh stromatolitov Sibiri* (Features of Formation and Distribution of Riphean Stromatolites in Siberia), Moscow: Nauka, 1975.
- Skopintsev, B.A., *Formirovanie sovremennogo khimicheskogo sostava vod Chernogo morya* (Formation of the Present-Day Chemical Composition of the Black Sea Waters), Moscow: Gidrometeoizdat, 1975.
- Sorokin, Yu.I., *Chernoe more. Priroda i resursy* (The Black Sea: Nature and Resources), Moscow: Nauka, 1982.
- Sovetov, Yu.K., The Alluvial Deltaic System in the Late Precambrian of the Lesser Karatau and Talas Ranges in *Dokembriiskie i fanerozoiskie skladchatye oblasti* (The Precambrian and Phanerozoic Folded Zones), Frunze, 1989, p. 73.
- Teodorovich, G.I., *Litologiya karbonatnykh porod paleozoya Uralo-Volzhskoi oblasti* (Lithology of Paleozoic Carbonate Rocks in the Urals-Volga Region), Moscow: Akad. Nauk SSSR, 1950.
- Wilson, J.L., Carbonate Facies in Geological History, Berlin: Springer, 1975. Translated under the title *Karbonatnye fatsii v geologicheskoi istorii*, Moscow: Nedra, 1980.
- Volkov, I.I., The Distribution of Free Hydrogen Sulfide in the Black Sea Sediments, *Dokl. Akad. Nauk SSSR*, 1960, vol. 134, no. 3, pp. 676–679.
- Volkov, I.I. and Sevast'yanov, B.F., Redistribution of Chemical Elements in the Diagenesis of Black Sea Sediments, in *Geokhimiya osadochnykh porod i rud* (Geochemistry of Sedimentary Rocks and Ores), Moscow: Nauka, 1968, pp. 134–183.

Manganese Deposits of Georgia:

Communication 1. Geological Features and Isotopic Composition of Carbonate Manganese Ore from the Chiatura and Kvirila Deposits

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Abstract—Carbonate manganese ore from the Chiatura and Kvirila deposits is characterized by a wide variation in isotopic compositions of carbon ($\delta^{13}\text{C} = -34.5$ to -7.3%), oxygen ($\delta^{18}\text{O} = 18.9$ to -35.0%), and sulfur ($\delta^{34}\text{S} = -19.0$ to -41.2%). However, various (cryptocrystalline, crystalline, pseudo-oolitic, pseudopisolitic, and stringer) types of carbonate ores and the carbonate cement of oxide ore are close to each other in isotopic characteristics. Lithological, mineralogical, and isotopic data testify to the authigenic origin of manganese ore.

The origin of manganese deposits of Georgia has been a matter of considerable debate for a long time. Above all else, the discussion concerns the largest Chiatura deposit, which is currently mined and the most comprehensively studied from the standpoint of lithology, mineralogy, geochemistry, and geology.

Since the first systematic research of the Chiatura deposit under the supervision of A.G. Betekhtin, A.G. Avaliani, N.M. Strakhov, and their followers (Avaliani, 1982; Betekhtin, 1946; *Chiaturskoe* ..., 1964; Shterenberg, 1985, 1988; Strakhov *et al.*, 1968, and others), the concept of the sedimentary ("typical sedimentary," "sedimentary proper," "classic sedimentary") origin of manganese ore was predominant. According to these authors, the exogenic material that came into the ore-forming depression from the land served as a source of ore. Sapozhnikov (1967) suggested that Mn was introduced into the shallow-water environment by fluxes upwelling from deep hydrosulfuric zones of the Maikop paleobasin.

Dzotsenidze (1965, 1980) critically revised the popular sedimentary model and proposed a volcanogenic (hydrothermal) sedimentary hypothesis that considered the hypogene hydrothermal solutions to be a source of manganese and silica. This hypothesis was developed by many of his followers (Gogishvili *et al.*, 1980, 1982; Khamkhadze, 1981, 1986; Lekvinadze *et al.*, 1967; Machabeli and Khamkhadze, 1979; Machabeli, 1986; Makharadze, 1972, 1979; Merabishvili *et al.*, 1979; Mstislavskii, 1985, 1989, and others).

Without going into all of the pros and cons of one or another hypothesis thoroughly discussed in the literature, we note only that neither of them gives unambiguous answers to many questions concerning the deposit

location, the time of ore deposition, the ore material source, etc. At the same time, there are unequivocal geological arguments in favor of both alternative viewpoints. This obvious paradox indicates a different mode of manganese deposit formation, which in some aspects matches existing genetic ideas. Elision may be such a process.

The theoretical possibility of catagenic manganese ore deposition in elisional depressions was originally argued and applied to the Mangyshlak and Laba deposits by Kholodov (1982). Dvorov and Sokolova (1987) later came to the same conclusion regarding the Mangyshlak deposit. However, ordinary catagenic and elisional processes, which are not related to oil and gas formation are apparently unable to provide the concentrations of components required for ore generation, particularly for the formation of manganese deposits. Only petroleum water enriched in carbon dioxide, methane, hydrogen sulfide, and other aggressive components probably enables the leaching of a great amount of ore elements from country rocks and transporting them toward the surface (*Paragenesis* ..., 1990).

This concept was recently developed by Pavlov and Dombrovskaya (Pavlov, 1989; Pavlov and Dombrovskaya, 1993; *Paragenesis* ..., 1990), who established spatial and genetic links of deposits of Mn, Fe, etc. with oil- and gas-bearing depressions.

We have studied the carbon, oxygen, and sulfur isotopic compositions in various types of manganese ores at the well-known Georgian deposits, taking into account their geological setting and composition. The first attempt to reconcile isotopic, lithological and mineralogical data with geological characteristics of adjacent oil- and gas-bearing depressions was undertaken.

This provided a new insight into the origin of manganese ore deposits in Georgia and elsewhere.

GEOLOGIC SUMMARY OF THE CHIATURA AND KVIRILA DEPOSITS

The Chiatura deposit embodying enormous reserves of high-quality manganese ore, the spatially related Kvirila deposit, and some smaller manganese deposits and occurrences are localized in shallow-water coastal sediments of the Oligocene–Lower Miocene Maikop Group near the Dzirula Crystalline Massif. Sedimentary sequences with a total thickness of many kilometers were deposited in depressions to the west and east of the Dzirula Massif from Early Mesozoic to Recent. More deep-water facies are also known among these deposits, including the Maikop Group.

The Maikop Group represents a specific facies of dark gray and brown schistose clays and sandstones, locally strongly enriched in jarosite and containing marl and siderite nodules (Laliev, 1964). Clays are predominant, whereas sandstones occur only locally. In the Chiatura district, the sandstone–siltstone facies is known only in its southwestern ore-bearing part; the thickness of sandstones and siltstones decreases northeastward, and they are gradually replaced by typical Maikop clay of noticeably increased thickness.

Manganese ores occur as subhorizontal layers within the Maikop Group and are confined to the Khadum Stratum in its lower part.

The ore stratum overlies foraminiferal limestone or limy sandstone of Upper Eocene at the Kvirila deposit and Upper Cretaceous limestone at the Chiatura deposit. The Maikop Group is overlain by the Tarkhan Stratum of Middle Miocene represented by clayey and sandy deposits, 100 m thick, or by marls and sandy deposits of the Chokrak Stratum, up to 50 m in thickness.

Mode of Manganese Ore Occurrence at the Chiatura and Kvirila Deposits

The Chiatura deposit is situated at a high plateau with elevations of 430–800 m dissected by deep canyons of the Kvirila River and its tributaries into separate highlands; Darkveti, Itkhvisi, Mgvimevi, Shukruti, Perevisi, Merevi, and Pasietsi highlands are the largest ones.

The orebody has a spherical triangular shape (Betekhtin, 1946); at the southwest, it is limited by the northwestern Main Fault, strikes for 12.5 km to the northeast, and gradually pinches out (Fig. 1).

Manganese ore makes up a subhorizontal stratiform lode; its thickness varies from 2–4 m in the southwestern part of the deposit near the Main Fault to 4.5–5.5 m in the central part and 14 m in northeastern parts of the deposit. The Mn ore mineralization forms a series of lenticular layers of various thickness and length embedded into the host sandy silt stones. These layers

are chaotically interconnected both in vertical and lateral directions giving rise to a mesh structure of the sequence (Strakhov *et al.*, 1968).

Subore, ore, and supraore strata are recognized at the deposit (Betekhtin, 1946). The subore horizon overlies the Upper Cretaceous limestone and is represented by fine-grained sand or slightly cemented sandstone; its thickness increases from 0.1 m on the southwest to 30 m on the northeast of the deposit. The sand is of arkosic quartzose composition. The supraore horizon, 25–30 m in thickness, consists of opoka and spongolite on the southwest; on the northeast it is replaced by the Maikop clay, 70–80 m thick. The upper part of the supraore horizon locally hosts the second ore horizon of subeconomic importance (Edilashvili *et al.*, 1973a, 1973b; Shterenberg, 1985).

The Kvirila deposit is located to the southwest of the Chiatura deposit and occupies a major area of the Kvirila depression. The depression is a wide graben-syncline with horizontal beds in its center and minor folds and faults at limbs. The depression is bounded by faults on all sides. Is separated from the Okriba land on the north by the Sachkheri Fault and from the Adzhar-Trialet Fold Zone on the south by the Suram–Gokeshuri Fault. The Chkhari Fault serves as a boundary between the depression and the Dzirula Massif, and the Chishuri Fault—as a divide between the Kvirila and Rioni depressions (Tumanishvili, 1989). Following Edilashvili *et al.* (1973a, 1973b, 1980) the northern and southern sublatitudinal faults represent thrusts that inherited long-living faults. Jurassic and Cretaceous deposits are thrust along these faults over Paleogene rocks.

The Mn ore layer occurs in the lower part of the Oligocene silty-clayey unit, which overlies Upper Eocene foraminiferal marl replaced by limy sandstone. In the inner part of the basin the ore layer is subhorizontal and lies at a depth of 400–700 m (the attitudes of the ore layer floor are of –400...–500 m). At the depression walls the layer is steep and crops out.

The ore layer is discontinuous and is subdivided into several sites. At the northern and northwestern margins of the basin, the ore layer is exposed as a strip, 20 km long and 0.5–1.5 km wide known as the Chkhari-Adzhameti deposit (Fig. 2). Here, the Mn ore body, 0.6–3.0 m thick, is oxidized and contains only relics of carbonate material. The Vani–Zestafoni ore-bearing strip at the southern margin of the Kvirila Depression extends for 35 km. The ore stratum, 7.0–8.5 m thick, is represented here by thin (0.1–0.3 m) lenticular bodies of low-grade carbonate and oxidized ores. Isolated lenses and concretions of siderite and manganosiderite, less frequently oligonite are encountered within the Maikop Group clay at the ore stratum level (Makharadze and Chkheidze, 1971). Above the ore level, the concretions are mainly composed of calcite, occasionally with a dolomite admixture.

The Terdzholi, Cholaburi, Rodinauli, Adzhameti, and Rokiti sites are delineated in the central part of the

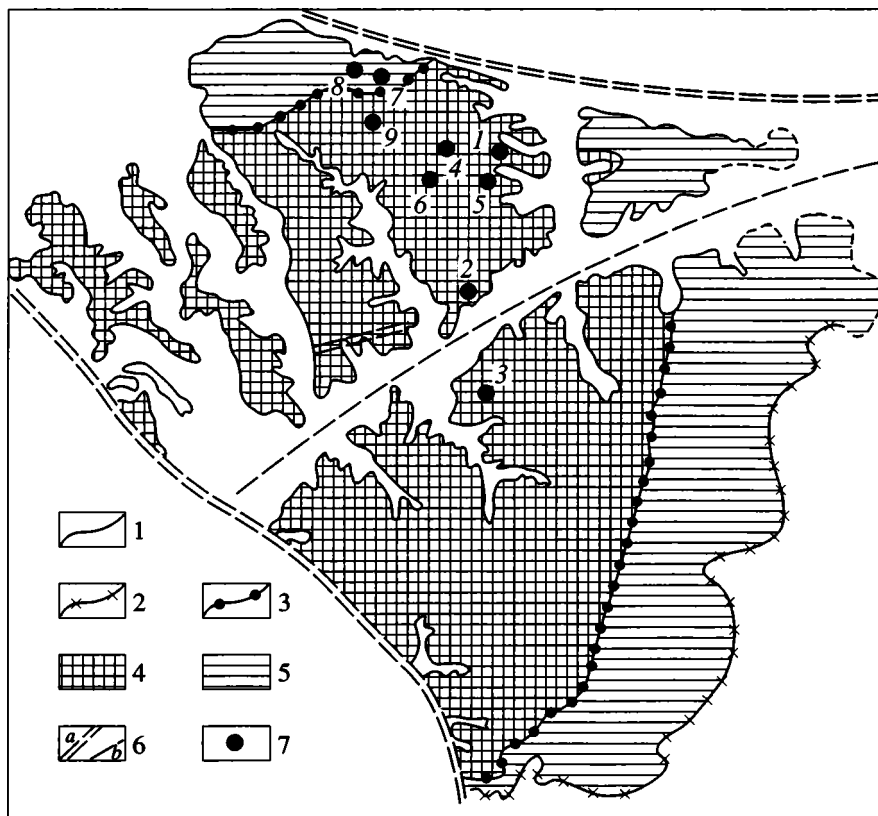


Fig. 1. Plan of orebody at the Chiatura manganese deposit, after *Chiaturskoe ...* (1964), Strakhov *et al.* (1968), Tabagari (1984). (1) Present-day limit of ore field; (2) contour of zero thickness of ore stratum; (3) oxide ore boundary; (4) area of joint occurrences of oxide and carbonate ores; (5) ore carbonate area; (6) faults: (a) proven, (b) inferred; (7) isotop sampling stations: (1) Darkveti Highland, site 4, open pit; (2) Darkveti Highland, site 8, open pit; (3) Akhali-Itkhvisi Highland, adit; (4) Darkveti Highland, site 3, adit; (5) Darkveti Highland, site 8, adit; (6) Darkveti Highland, site 10, adit; (7) Darkveti Highland, borehole 830; (8) Darkveti Highland, Borehole 826; (9) Darkveti Highland, Borehole 832.

depression. The highest ore concentration is typical of the Rodinauli and Cholaburi sites (Fig. 2). Mineralized areas in the central part of the basin are separated from the ore occurrences of the Chkhari-Adzhameti Zone by barren sites; both areas are connected only on the west in the Brolis-Kedi-Adzhameti district. Judging from reduced thicknesses (8–35 m) of Oligocene deposits, the barren areas are related to paleouplifts.

The manganese ore is embedded into the lower Maikop Group section; its thickness varies from 45–80 m in eastern and central parts of the depression to 250–300 m on the west and south. As at the Chiatura deposit, the terrigenous component of ore-bearing unit is represented by a sandy-silty material. The sandy facies proper occurs only on the north near the Okhriba land.

Subore, ore, and supraore strata are recognized both at the Kvirila and Chiatura deposits. The subore stratum, which consists of loose sand, is up to 3 m in thickness. Supraore deposits are represented by siliceous rocks (spongolites) at the bottom and clayey rocks at the top. The thickness of the supraore unit increases from 4–5 m on the east to 21–30 m on the west.

The orebody is built up by a stratiform lode, 0.2–5.8 m thick. The thickness is variable, and isolated ore occurrences (sites) are separated by barren or low-mineralized sectors. The greatest thickness of ore stratum is pointed out in the western part of the depression; in the central part it is reduced to 2–3 m, and the ore stratum pinches out to the east and south. The ore layer is characterized by a complicated structure due to the alternation of lenticular layers with various ore types and beds with variable contents of ore and nonore (terrigenous and authigenic) components. The ore layer at the Kvirila deposit is more compact as compared to the Chiatura deposit; the number of barren interlayers is substantially reduced.

The Kvirila deposit differs from the Chiatura deposit in postore geological evolution. The composition and thickness of Oligocene rocks give no evidence for any distinction in the duration of ore deposition and subsequent sedimentation during the Chokrak, Karagan, Konk, and early Sarmatian time. The seafloor submerged slowly, and the total thickness of the Oligocene–Early Sarmatian sequence attained 200–250 m in both districts. Beginning in the Middle Sarmatian,

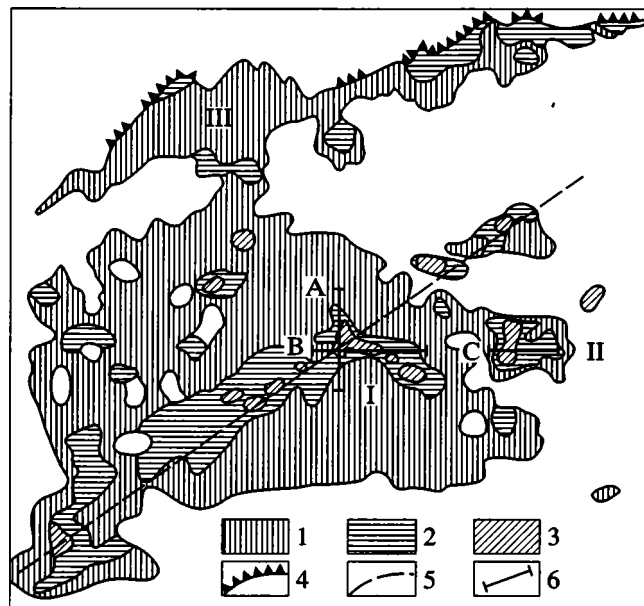


Fig. 2. Plan of manganese ore stratum in the Kvirila Depression, after Dolidze *et al.* (1980), Khamkadze and Tumanishvili (1984). Mineralization parameters, metroperecents: (1) 0.1–10, (2) 10–30; (3) >30; (4) Manganese ore outcrops; (5) fault suggested to be ore-feeder for Rodinauli and Cholaburi sites; (6) borehole profiles sampled for isotopic studies: (A) boreholes 814, 518, 824 (from north to south); (B) boreholes 518, 536 (from west to east); (C) boreholes 868, 889 (from west to east). Sites: (I) Rodinauli, (II) Cholaburi; (III) Chkhari-Adzhameti occurrence ore zone.

the Chiatura and Kvirila Depressions evolved in different fashions. The Chiatura district was uplifted above the sealevel. At present, the ore stratum floor occurs at an elevation of 630–800 m above the sealevel. The Kvirila basin continued to subside, and the ore stratum floor turned out to lie at a depth of 550–600 m beneath the present-day surface, i.e., 400–440 m below the sealevel. Thus, the vertical displacement of ore layers at Chiatura and Kvirila deposits reached more than 1000 m.

Types of Manganese Ore, Their Structures, Textures and Paragenetic Mineral Assemblages

Host rocks and authigenic mineralization. Host rocks at the Chiatura and Kvirila deposits are represented by sandy-silty rocks of the Maikop Group. These rocks are composed of quartz predominant and subordinate feldspars (microcline, orthoclase, plagioclase). Other minerals (micas, amphiboles, accessories), organic remnants (wood, fish skeletons and scales), lithic and vitric fragments are present in insignificant amounts.

The manganese mineralization within the Maikop Group terrigenous rocks is clearly confined to areas with intensely developed authigenic siliceous and zeolite mineralization (Khamkhadze, 1981; Machabeli, 1986; Makharadze, 1972, 1979). Manganese minerals, also authigenic, are closely (paragenetically) associated with the latter mineralization. The authigenic mineralization is most intense along faults, where the altered rocks (up to 90 m in thickness) may be used as

fault tracers. The intensity of secondary mineralization is reduced with increasing distance from the fault, and a gradual transition to unaltered terrigenous rocks of the Maikop Group takes place.

The authigenic mineralization in fault zones is extremely diverse. Opal and clinoptilolite are especially widespread; montmorillonite, glauconite-type mixed-layer mica-montmorillonite minerals, phosphates, barite, gypsum, native sulfur, pyrite, marcasite are frequent. Solid bitumens are also abundant at authigenic mineral occurrences.

Silica in rocks with authigenic mineralization is commonly represented by opal and less frequently by chalcedony, and thus opoka, opalolite and spongolitic sandstone sites are formed. Opoka and opalolite are usually developed in the lower part of ore-bearing sequence, whereas spongolitic sandstone is encountered in the upper part; however, isolated sponge spicules are observed throughout the whole section. The primary chemogenic nature of siliceous biogenic material was justified by Makharadze (1979) and Khamkhadze (1981). Opalolite commonly contains a clayey admixture as rounded segregations, which are composed of opal, of clay material, or of both. The Mn ore material preferentially replaces opoka and opalolite, which are the most porous and permeable. The more massive and low-permeable spongolitic sandstone commonly makes up the roof of ore stratum.

The additional, constant and widespread component of the Mn ore is represented by zeolites. They occur

throughout the whole ore bearing unit, however, the highest content was pointed out in the upper part of ore stratum and in supraore deposits where zeolites often become major rock-forming minerals (up to 60–65%) (Gogishvili *et al.*, 1979; Merabishvili *et al.*, 1979) and form separate units, up to 20 m thick. According to (Butuzova, 1964), it is not mandatory that zeolites, which are represented by the silica-rich clinoptilolite, must be spatially and genetically related to volcanogenic material, as was previously assumed by many researchers.

The authigenic non-metalliferous mineralization is much more abundant at the Kvirila deposits than at the Chiatura deposit, especially in its central and southwestern parts (Khamkhadze, 1981; Machabeli, 1986; Makharadze, 1972; Merabishvili *et al.*, 1979). This mineralization comprises not only ore and supraore units, but also underlying Upper Eocene marls, sharply suppressing the terrigenous rock component. Upper Eocene marl (Khamkhadze, 1981) is dolomitized, silicified, montmorillonitized and zeolitized; at the southwestern margin it is almost completely replaced by the opoka.

In addition to terrigenous and authigenic components, the volcanic materials represented by ash, tuff, and tuffite were reported from Lower Oligocene rocks and underlying Upper Eocene marl in the Kvirila Depression (Makharadze and Chkheidze, 1971). These authors have noted that the vitric material is commonly replaced by montmorillonite, clinoptilolite, and opal; because of this, the ash texture was lost, and the volcanogenic nature of above-mentioned minerals is difficult to recognize. We observed only scarce particles of fresh, unaltered volcanic glass, and therefore the abundance of volcanic material remains ambiguous.

The ore layer structure and ore types. Primary and oxidized Mn ores are distinguished. We consider only primary ore, which is not altered under supergene conditions. The manganese is represented in this ore by oxides and carbonates, and depending on their contents, the oxide, oxide-carbonate, and carbonate ore types are recognized. According to our observations, the silicate manganese mineralization, particularly neotocite and braunite in association with hausmannite, also occurs at deposits under discussion. The occurrence of these minerals in Borehole 889 at the Kvirila deposit cannot be related to the metamorphism of ore due to basalt injections as it takes place at the Chiatura deposit (Avaliani, 1982; Betekhtin, 1946; *Chiaturskoe* ..., 1964), because basalts are lacking at the Kvirila deposit.

At the Chiatura deposit, the oxide ore is developed in its southwestern part near the Main Fault and in the central part close to the Kvirila River. In outer parts of the deposit they are replaced by carbonate ore. Two main ore members, distinct in structure and composition, were recognized in vertical section until recent time (Betekhtin, 1946; *Chiaturskoe* ..., 1964; Shterenberg, 1985). The lower ore member plays a leading role

and is mainly composed of psilomelane¹ and pyrolusite; toward the margins of the deposit they are replaced by manganite and then by carbonate ore. The upper member is largely represented by carbonate ores with thin interlayers and lenses of oxide ore. Tabagari (1980, 1984) has traced one more carbonate ore member, which is located beneath the two above-mentioned members.

The facies zonation in distribution of ore types was noted at the Chkhari-Adzhmeti site of the Kvirila deposit (Avaliani, 1982). Oxide psilomelan-pyrolusite ore with a manganite admixture is replaced southward first by the oxide-carbonate and then by the carbonate ore. Autonomous manganite layers are lacking in this part of the depression. The central part of the depression has been studied only from boreholes, and a zonation of this area remains obscure. The carbonate ore only was found in the southern Vani-Zestafoni of ore occurrence zone. As at the Chiatura deposit, most complete sections comprise lower carbonate, middle oxide and upper carbonate ore members. The middle member is often either represented by an oxide-carbonate ore or is absent; a common layer of carbonate ore exists in this case.

Thus, the oxide ore is surrounded by carbonate ore from lower, upper, and pinch out zones, and such replacements can hardly be explained by a facies change.

Following the textural and structural features, oxide ores are divided into the oolitic (granular²) and massive (plasti²) ores. Oolitic ores are divided into ores with hard siliceous (zhgali²) and hard calcite cement (mtsvari²), as well as the lump-oolitic ore (satskhili²) with angular aggregations. The massive (plasti²) ore has an oolitic fine-grained massive texture.

Carbonate ores are divided into massive and disseminated (granular) varieties. Massive ore has a fine-grained massive texture; the disseminated ore is characterized by rounded segregations, 0.5–8.0 mm in diameter. Following our observations, these varieties resulted from the replacement of either the massive host rocks or the rocks containing rounded clay-opal inclusions by a carbonate material (Fig. 3).

The variable composition of manganese carbonate ore depends on the degree of such a replacement. As has been shown by our studies, the carbonate content ranges from 0 to 89%. The chemical composition of carbonate and oxide-carbonate ores containing more than 20% of carbonate materials is given in Tables 1 and 2. MnCO₃ is a predominant carbonate; its content varies from 12.75 to 81.49% and prevails over CaCO₃ content for 2–15 times. A small amount of MgCO₃ (up to 5%) was noted in some samples. The silica content in host rocks is significant (60–90%), whereas in the ore, it is reduced to 3.36–45.5% because of the increase

¹ Here and further the term "psilomelan" designates a mixture of finely dispersed, often X-ray-amorphous minerals represented by manganese oxides and hydroxides.

² Local names.

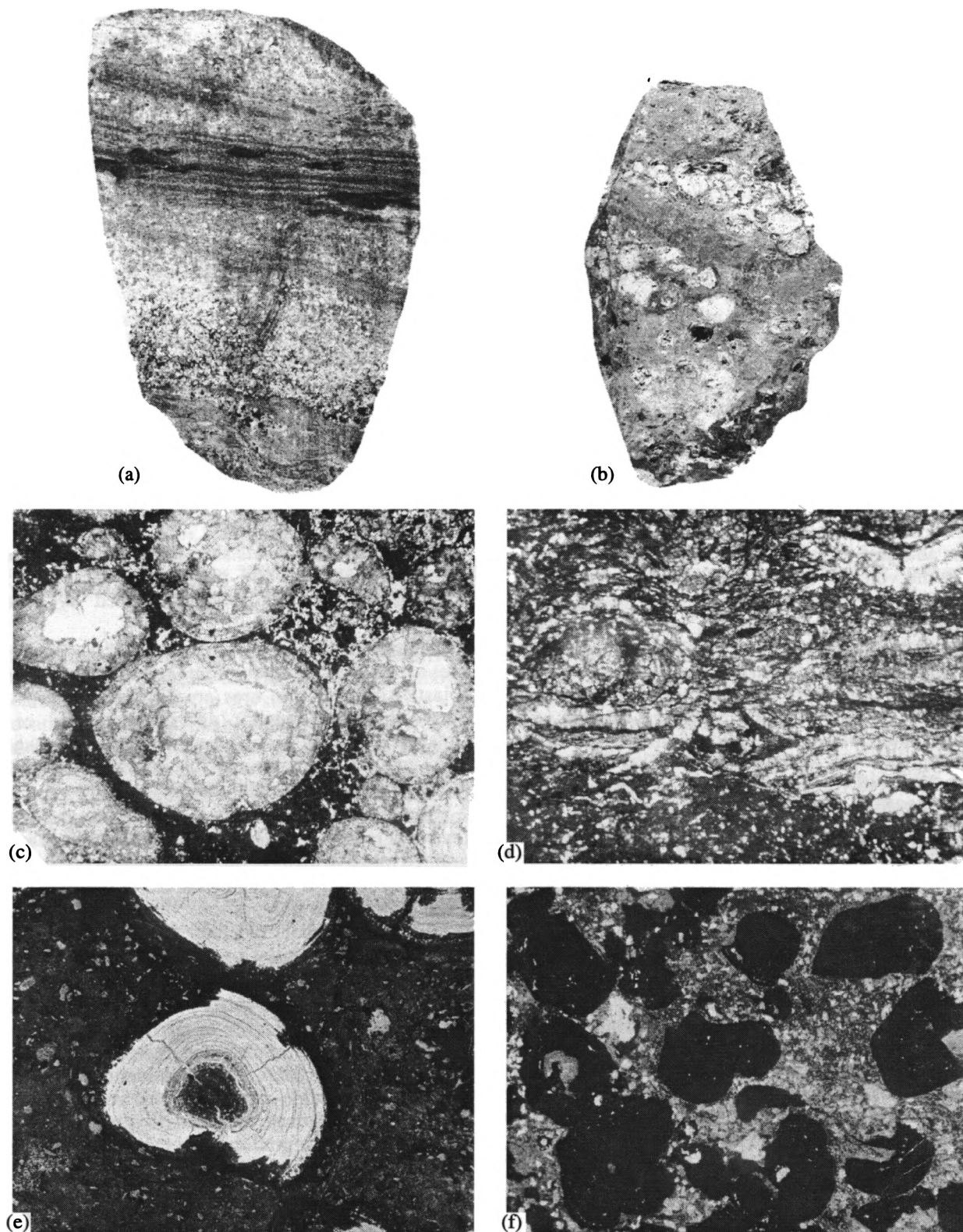


Fig. 3. Textural and structural features of manganese carbonate ore from the Chiatura deposit. (a, b) Disseminated ore; lumps, dimin 1.15 and 1.23, respectively; white is oolite-type carbonate segregations replacing primary opal inclusions; gray is cryptocrystalline carbonate cement; black lenses are solid bitumen inclusions; (c) spherulitic aggregates of manganese carbonate replacing the opal segregations with terrigenous quartz grains; thin section, magn. 96, parallel polars; (d) ribbon veinlet structure of recrystallized Massive carbonate ore; thin section, magn. 14.5, crossed polars; (e, f) replacement of oolitic manganite ore by manganese carbonate: (e) polished section, magn. 14.5; (f) thin section, magn. 14.5, parallel polars.

in carbonate content. As a rule, the contents of other components in carbonate ore do not exceed a few percent age points.

Manganese carbonate ores from the Chiatura and Kvirila deposits are close in composition (Tables 1 and 2). Higher values of CaO and BaO maximums at the Chiatura deposits and Fe_2O_3 and P_2O_5 maximums at the Kvirila deposit can only be regarded as exceptions.

The complex investigation of carbonate ore has shown that it consists of a mixture of minerals belonging to the calcite-rhodochrosite isomorphic series with a small admixture (up to 5–6%) of kutnahorite—a manganese carbonate of a dolomite structure. Dolomite, oligonite, and siderite occasionally occur in insignificant amounts. Judging from the intensity of 1014 reflections on X-ray patterns, most samples represent complex mixtures with rhodochrosite and manganocalcite being predominant. In addition to carbonates, terrigenous minerals (quartz, feldspars, micas), lithic and vitric fragments, as well as authigenic minerals, such as opal, zeolites (clinoptilolite), glauconite, glauconite-smectite mixed-layer minerals, neotocite, pyrite, barite, gypsum, native sulfur, bitumens, were identified in thin sections and determined with X-ray and thermic analyses.

Manganese carbonate ores from the Chiatura and Kvirila deposits are close to each other in mineral and chemical composition, structural and textural features, and physicochemical properties. Both ore types are characterized by a pronounced heterogeneity. Variations in ore composition, texture, and density are revealed by visual examination of specimens and by microprobe study with a high magnification. This is a result of not only the primary nonuniform distribution of carbonate material in the host rock, but also of its subsequent diagenetic redistribution and alteration.

The five main modes of carbonate material occurrence were established on the basis of visual and microscopic observations. In accordance to this, the following groups of carbonate materials were selected for isotopic studies: (I) dark gray to black cryptocrystalline material from the opal-carbonate groundmass; (II) light gray to white loose, porous, frequently fine- and coarse-spherulitic material from the altered groundmass; (III) white, pink, greenish gray coarse-spherulitic material from rounded inclusions of pseudo-oolite and pseudopisolite types; (IV) light gray, white, pink crystalline material from veinlets; (V) gray, pink, coarse-spherulitic material from the cement of oxide-carbonate ore.

Group I comprises the earliest fine carbonate material mixed with silty and opal-zeolite components of the host rock, which are distributed in extremely irregular fashion. The cryptocrystalline carbonate in a combination with host material makes up solid segregations of dark gray or black color. If the host rock has an impregnated structure and contains round inclusions of opal or clay, then the carbonate material replaces only the rock matrix, while the inclusions retain their primary composi-

tion. The carbonate material of this group is commonly represented by rhodochrosite or Ca-rhodochrosite.

Group II includes later carbonate material that resulted from the dissolution and redistribution of carbonates from the group I and host rocks. In this case, the ore becomes porous and often loose. Opal and clay inclusions are also affected by leaching. The carbonate material around pores and partly within them is commonly devoid of admixtures, but contain concomitant authigenic pyrite, barite, zeolite grains. New-formed light-colored fine-, medium-, and coarse-spherulitic carbonate aggregates stand out against the background of older dark gray material. The carbonate material of this group is represented by a mixture of rhodochrosite or Ca-rhodochrosite with manganocalcite.

Group III comprises the carbonate material of rounded inclusions (pseudo-oolites and pseudopisolites) from disseminated carbonate ore, which were formed due to the replacement of primary opal or clay inclusions by a carbonate. The process was accompanied by their partial or complete leaching. As a result, some cells remained empty, some partially retained the original material, and others were partially or completely filled with carbonate. The latter is commonly coarse-spherulitic due to the crystallization in a free space. It should be noted that rounded inclusions in carbonate ore are entirely devoid of concentric layering typical of oolites and pisolites, which are widespread among oxide and oxide-carbonate ores. Carbonate inclusions only inherit the shape of primary opal-clay segregations. Their light white, pink, and greenish gray colors stand out against the country rock. The carbonate material in inclusions is represented by rhodochrosite or calcite. The formation of carbonates from groups II and III are probably closely related.

Group IV represents the carbonate material from veinlets in the carbonate ore. Both stratal and cross-cutting veinlets occur; they are always composed of clearly crystalline carbonate, frequently forming featherlike aggregates, rosettes, and ribbons. The thickness varies from parts of one millimeter to a few millimeters in cross-cutting veinlets and may attain several centimeters in stratal veinlets; the latter are usually lenticular and pinch out for a certain distance. These veinlets pull apart the host rocks and compress the adjacent layers; consequently, bulges, lenses, augen texture arise. Veinlets are composed of light gray, white or pink carbonate material. Stratal veinlets are commonly represented by rhodochrosite or Ca-rhodochrosite, whereas the cross-cutting veinlets consist of calcite or manganocalcite.

Group V is represented by a carbonate cement of oxide-carbonate ore, which is abundant in the middle part of the ore unit. The carbonate, silty, and opal-zeolite materials make up the matrix that embodies segregations, 2–10 mm in size, commonly composed of manganite and occasionally of pyrolusite, goethite, or neotocite. These segregations are generally corroded

Table 1. Chemical (wt %) and mineral compositions of manganese ore and host rocks from the Darkveti and Itkhvisi highlands, the Chiatura deposit

Rock and ore lithotypes	Sample no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁻	H ₂ O ⁺	CO ₂	BaO	SrO
Darkveti Highland															
C	20	13.31	0.12	2.97	0.74	37.94	2.36	7.81	0.28	0.49	1.08	0.72	29.73	0.015	0.016
C	17	19.54	0.12	2.24	0.35	27.19	1.90	15.49	0.23	0.43	1.03	0.91	28.32	0.082	0.019
C	109	16.63	Tr.	0.62	0.67	31.88	4.90	10.00	0.11	0.15	1.53	1.81	27.56	0.72	–
C	108	23.80	Tr.	3.20	1.13	30.55	2.17	7.15	0.43	0.46	1.18	1.21	24.87	0.30	–
C	19	20.10	0.12	2.98	2.75	28.14	2.21	12.08	0.23	0.72	2.21	0.29	25.16	0.43	0.02
O	22	15.86	–	2.74	0.91	4.28	0.56	3.74	0.20	0.47	2.23	2.15	3.56	1.19	0.049
C–O	23	12.74	–	3.43	1.62	26.02	1.01	4.59	0.24	0.56	1.48	7.20	7.06	2.70	0.076
C–O	28	18.61	0.12	5.99	1.60	24.84	1.20	6.27	1.32	0.72	1.93	5.63	8.57	1.19	0.043
C–O	27a	9.37	–	2.38	0.74	24.72	0.80	11.69	0.20	0.37	1.00	7.35	10.79	1.76	0.048
C	24	4.05	–	1.44	0.15	49.05	1.15	3.39	0.06	0.20	1.38	5.52	32.78	0.009	0.005
Op–C	26	36.67	0.12	4.37	0.58	23.63	1.18	5.97	0.36	0.74	2.41	2.07	18.11	0.02	0.019
Itkhvisi Highland															
C	144	3.93	–	1.24	1.21	34.57	1.62	20.64	0.16	0.17	0.79	0.73	33.96	0.01	0.031
C	145	7.22	–	1.87	–	35.14	2.10	14.15	0.15	0.27	0.79	1.07	34.20	0.03	0.02
C	147	7.52	–	2.23	0.48	33.61	1.68	17.71	0.19	0.29	0.89	0.98	33.52	0.04	0.019
C–O	149	10.69	–	3.64	1.14	29.64	1.35	6.29	0.16	0.40	0.75	7.15	12.99	0.054	0.02
Op–C	150	41.13	0.29	7.69	1.45	16.39	1.75	8.74	0.64	1.43	2.00	2.89	14.05	0.17	0.046
Op–C	153k	23.42	–	3.53	0.59	28.70	8.80	7.90	0.29	0.71	2.50	2.65	22.70	0.17	0.033
O	153m	18.90	–	3.30	3.08	26.25	0.87	0.87	0.18	0.61	2.20	8.11	1.20	3.10	0.072
S	155	59.42	0.39	8.27	1.66	8.47	1.72	5.41	0.85	1.91	1.24	3.86	5.80	0.31	0.05

Table 1. (Contd.)

Rock and ore lithotypes	P ₂ O ₅	MnO ₂	Total	SO ₃	Fe _{py}	S _{py}	MnCO ₃	CaCO ₃	Total carbonate	Manganite	Pyrolusite	Neotocite	Opal + quartz	Montmorillonite, glauconite, zeolite
Darkveti Highland														
C	—	—	99.32	0.25	0.69	0.80	61.46	14.10	75.56	—	—	—	8	9
C	—	—	100.00	1.05	0.51	0.59	41.97	27.73	69.70	—	—	4	16	7
C	0.29	2.16	99.35	0.32	—	—	51.65	17.68	69.33	—	2	—	7	16
C	0.14	1.90	99.38	0.89	—	—	49.49	10.96	62.55	—	2	—	14	12
C	—	—	98.88	0.23	0.56	0.35	40.77	21.52	62.39	—	—	9	14	5
O	—	60.96	99.65	0.75	—	—	1.59	6.69	8.28	8.22	56.87	—	7	15
C—O	—	29.33	99.46	1.20	—	—	8.95	8.21	17.16	51.05	3.91	—	3	17
C—O	0.08	22.20	100.05	0.74	—	—	13.07	11.22	24.29	38.32	3.12	—	7	19
C—O	—	37.92	100.04	0.90	—	—	4.05	20.93	24.98	51.47	2.29	14	6	8
C	—	—	100.12	0.05	0.41	0.48	78.56	6.07	84.63	—	—	2	3	3
Op—C	—	—	100.39	0.89	1.51	1.74	34.95	10.69	45.64	—	—	6	30	16
Itkhvisi Highland														
C	—	—	99.88	0.15	0.31	0.36	46.07	36.95	83.02	—	—	16	—	—
C	0.37	1.01	99.82	—	1.43	—	56.93	25.32	84.60	—	1	—	5	5
C	—	—	99.49	—	0.15	0.18	50.97	31.70	82.67	—	—	16	—	—
C—O	—	26.12	100.06	0.17	—	—	20.93	11.26	32.19	41.66	5.37	—	7	10
Op—C	—	—	99.21	0.10	0.20	0.24	18.69	15.63	34.32	—	—	14	30	25
Op—C	0.75	1.28	99.39	—	1.37	—	43.92	13.37	57.29	3.18	—	—	20	10
O	0.70	30.12	100.33	0.77	—	—	1.33	1.56	2.89	60.54	—	3	15	12
S	—	—	99.45	0.09	—	—	13.72	1.25	14.97	—	—	—	47	30

Note: Analyses were performed in the chemical laboratory of the IGEM. Analysts: L.S. Tsimlyanskaya, M.S. Obolenskaya, G.E. Kalenchuk, E.P. Frolova. Analyses are listed downward the geological section. Lithotypes. *Manganese ore*: (C) carbonate, (O) oxide, (C—O) carbonate—oxide, (O—C) oxide—carbonate, (Op—C) opal—carbonate, (N) neotocite, (N—C) neotocite—carbonate; *other rocks*: (G—C) goethite (hematite)—carbonate, (Cl—C) clay—carbonate, (G—Op) goethite (hematite)—opal, (Op—Cl) opal—clay, (Cl—Op) clay—opal, (G—Cl) goethite (hematite)—clay, (S) sandstone, (SS) spongolitic sandstone, (Ph) phosphorite. The dash denotes the absence of element or mineral.

Table 2. Chemical (wt %) and mineral compositions of manganese ore and host rocks from the Rodinauli (boreholes 824, 814, 518, 808, 536) and Cholaburi (boreholes 889, 868) sectors of Kvirila deposit

Rock and ore lithotypes	Sample no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁻	H ₂ O ⁺	CO ₂	BaO
Borehole 824, ore interval 607.0–607.8 m														
Op-C	27	33.90	0.23	3.56	2.90	23.17	1.95	8.26	0.86	0.78	0.97	1.74	20.80	0.03
C	26	15.37	0.27	4.07	2.88	32.61	3.71	7.82	0.74	0.75	1.34	1.84	27.68	0.03
C	25	14.82	0.23	3.44	3.70	34.50	2.58	7.88	0.59	0.50	1.43	1.26	29.12	0.02
Op-Cl	24	60.22	0.55	10.86	4.96	0.05	2.25	1.75	1.96	2.63	4.87	3.71	–	0.013
Borehole 889, ore interval 584.8–587.4 m														
Op-Gl	45	68.24	0.72	9.12	7.28	0.043	1.88	0.86	1.56	2.32	3.65	3.47	–	0.019
C	44	3.45	0.10	1.18	4.11	50.30	1.79	2.87	0.20	0.19	0.54	0.51	34.75	0.408
N	43	28.36	0.54	8.50	5.08	25.90	8.75	0.87	0.85	0.32	4.64	8.67	4.36	0.008
N	42	28.38	0.35	6.14	4.02	29.48	7.60	2.25	0.75	0.50	3.65	9.04	2.80	0.008
O	39	10.83	0.18	1.85	0.90	42.60	1.39	0.32	0.40	0.019	1.33	7.98	5.36	0.009
O	37	16.53	0.25	4.07	2.78	37.99	3.61	0.14	0.30	0.04	1.50	5.00	0.52	0.64
C	34-2	18.81	0.22	3.46	1.59	29.52	1.18	12.47	0.82	0.67	0.95	1.73	22.09	0.086
Ph	34-1	4.59	0.15	1.02	1.40	2.96	0.52	52.20	1.14	0.41	0.65	2.27	6.80	0.13
Borehole 814, ore interval 549.1–550.6 m														
SS	55	84.69	0.14	3.49	1.59	0.37	0.88	1.07	0.57	0.55	1.73	1.57	–	–
C	54	30.80	0.13	2.51	2.92	24.26	1.94	9.46	0.53	0.35	0.93	1.90	22.90	–
Op-Gl	53	60.00	0.44	9.50	6.00	0.55	1.18	1.70	2.19	2.34	4.68	3.48	0.50	–
G-Cl	52	45.20	0.30	8.74	21.72	3.91	2.03	3.00	1.70	1.66	3.36	4.67	3.44	–
O-C	51	12.08	0.06	3.14	0.98	27.68	2.60	7.25	0.43	0.46	0.85	5.61	16.48	–
O-C	50-1	31.02	0.25	6.46	2.66	15.73	3.49	6.58	1.28	1.33	2.37	3.72	14.96	–
Op-C	50-2	37.50	0.60	7.94	3.09	17.50	3.23	6.20	1.63	1.47	1.45	3.62	14.78	0.05
G-Cl	49-1	38.73	0.38	9.38	28.66	4.05	2.07	2.12	1.69	1.91	3.37	5.00	2.74	–
N-C	49-2	21.31	0.43	4.26	10.95	22.62	3.42	9.38	0.90	0.83	1.47	3.41	20.70	0.016
Op-Gl	48-1	58.89	0.30	12.26	9.74	0.30	3.49	1.48	2.44	3.25	5.92	3.89	tr.	–
Op-Gl	48-2	52.30	0.71	10.14	14.88	0.30	3.67	1.78	2.07	2.47	4.97	5.64	–	0.036
Borehole 868, ore interval 576.3–577.7 m														
Op-Gl	66	61.93	0.46	9.78	9.43	0.057	2.32	1.94	1.68	2.67	4.23	4.08	0.23	0.03
C	64	3.36	–	0.50	1.72	45.31	1.50	10.75	0.24	0.15	0.31	0.85	34.91	0.02
N-C	63	15.68	tr.	4.74	4.20	27.72	3.40	11.42	0.85	0.67	2.26	2.24	25.40	0.027
C	62	11.01	tr.	3.91	3.36	30.68	2.87	12.88	0.63	0.42	2.43	1.58	29.49	0.023
Cl-C	61	24.41	0.48	6.58	7.56	21.80	3.39	6.33	1.09	1.35	4.29	3.49	16.40	0.03
C-Cl	60	45.50	0.61	8.89	4.50	7.87	2.50	7.12	1.72	2.09	3.75	3.84	8.84	0.043
C	59	19.43	–	4.10	3.29	25.92	2.37	12.77	0.69	0.56	1.01	1.99	21.90	0.012
Borehole 518, ore interval 576.0–577.0 m														
Op-C	74	30.53	0.18	3.43	7.42	22.04	2.60	7.07	0.56	0.46	1.35	1.17	22.62	0.006
O-C	72	7.15	–	1.96	1.26	36.19	2.89	8.71	0.47	0.51	0.70	2.30	29.43	0.02
O-C	70	13.11	tr.	3.29	1.88	31.53	2.53	6.52	0.73	0.52	1.43	3.78	21.83	0.03
G-C	69	27.52	0.40	6.92	19.28	15.62	2.57	5.10	1.29	1.21	2.70	4.08	12.74	0.05
Op-Gl	68	56.49	0.48	13.72	6.28	1.50	2.40	5.44	2.20	3.35	2.29	1.62	1.84	0.084
Borehole 808, ore interval 560.6–561.35 m														
C	81	18.18	0.18	4.31	3.48	26.32	2.10	13.18	0.70	0.57	1.42	1.68	23.45	0.0043
C	79	9.03	0.15	2.52	4.84	32.45	4.28	11.65	0.52	0.46	1.29	1.29	31.02	0.014
Borehole 536, ore interval 580.0–581.5 m														
C	87	26.16	0.27	6.16	4.56	21.65	2.95	9.83	1.05	1.20	1.83	1.83	21.67	0.009
N-C	85	24.03	0.31	6.98	4.98	31.81	3.42	5.26	1.09	0.90	2.08	4.03	14.15	0.047
C	84	21.90	0.22	5.08	7.74	20.46	3.29	11.67	0.86	0.87	1.83	1.89	22.05	0.0059

Table 2. (Contd.)

Rock and ore lithotypes	SrO	P ₂ O ₅	MnO ₂	Total	MnCO ₃	CaCO ₃	MgCO ₃	Total carbonate	Manganite	Pyrolusite	Neotocite	Opal + quartz	Montmorillonite, glauconite, zeolite	Phosphate
Borehole 824, ore interval 607.0–607.8 m														
Op-C	0.046	0.16	–	99.36	37.54	14.60	–	52.14	–	–	–	28	13	–
C	0.035	0.15	–	99.30	52.83	14.00	2.44	69.27	–	–	–	9	13	–
C	0.022	–	–	100.09	55.89	14.11	2.90	72.90	–	–	–	11	9	–
Op-Cl	0.08	0.15	–	98.92	–	–	–	–	–	–	–	30	65	–
Borehole 889, ore interval 584.8–587.4 m														
Op-Gl	0.025	0.30	–	99.49	–	–	–	–	–	–	–	42	52	–
C	0.006	–	–	100.01	81.49	5.14	2.46	89.09	–	–	–	2	3	–
N	0.017	–	3.02	99.89	11.38	–	–	11.38	–	–	88	–	–	–
N	0.019	1.35	3.81	100.17	7.31	–	–	7.31	–	–	85	–	–	4
O	0.009	–	25.94	99.12	13.99	–	–	13.99	52	–	26	–	–	–
O	0.007	–	26.08	99.46	1.36	–	–	1.36	52	–	40	–	–	–
C	0.075	5.57	–	99.24	47.82	8.60	–	56.42	–	–	–	9	20	14
Ph	0.31	25.81	–	100.37	4.80	11.26	–	16.06	–	–	–	2	6	66
Borehole 814, ore interval 549.1–550.6 m														
SS	–	0.19	–	9.60	–	–	–	–	–	–	–	76	15	–
C	–	0.78	tr.	99.41	39.30	16.93	–	56.23	–	–	–	20	17	–
Op-Gl	–	0.20	–	100.44	0.89	0.77	–	1.76	–	–	–	30	61	–
G-Cl	–	0.22	–	99.95	6.33	2.32	–	8.65	–	–	–	18	54	–
O-C	–	0.13	22.62	100.37	19.95	12.98	5.46	38.39	39	3	–	6	13	–
O-C	–	0.22	10.00	100.07	15.45	11.78	7.33	34.56	15	2	–	16	30	–
Op-C	0.09	0.38	–	99.53	16.32	11.11	6.78	34.40	–	–	21	25	10	–
G-Cl	–	0.23	–	100.32	–	3.79	2.04	5.83	–	–	12	18	39	–
N-C	0.057	–	–	99.76	24.87	16.79	7.18	48.84	–	–	21	10	9	–
Op-Gl	–	1.30	–	100.26	–	–	–	–	–	–	–	21	77	–
Op-Gl	0.045	0.41	–	99.42	–	–	–	–	–	–	–	15	74	–
Borehole 868, ore interval 576.3–577.7 m														
Op-Gl	0.044	0.47	–	99.35	–	–	–	–	–	–	–	30	64	–
C	0.02	–	–	99.64	68.96	19.24	–	88.20	–	–	8	–	–	–
N-C	0.026	0.40	–	99.04	32.99	20.44	7.14	60.57	–	–	21	5	7	–
C	0.024	tr.	–	99.30	49.70	23.06	–	72.76	–	–	–	1	20	–
Cl-C	0.05	2.05	–	99.30	353.2	6.54	–	41.86	–	–	–	5	39	5
C-Cl	0.051	2.63	–	99.95	12.75	8.99	–	21.74	–	–	–	27	38	6
C	0.045	5.53	–	99.61	41.99	13.23	–	55.22	–	–	–	12	15	14
Borehole 518, ore interval 576.0–577.0 m														
Op-C	0.019	–	–	99.46	35.70	12.66	4.97	55.97	–	–	–	24	13	–
O-C	0.03	–	7.58	99.20	48.68	15.59	6.07	72.29	15	–	–	3	8	–
O-C	0.039	–	12.33	99.55	34.91	11.67	5.31	53.32	25	–	–	6	14	–
G-C	0.052	–	–	99.53	22.73	9.13	–	31.86	–	–	5	15	21	–
Op-Gl	0.063	1.46	–	99.21	2.43	2.07	–	4.50	–	–	–	35	43	4
Borehole 808, ore interval 560.6–561.35 m														
C	0.060	3.24	–	98.87	42.61	16.19	–	58.83	–	–	–	10	16	8
C	0.045	–	–	99.56	52.57	20.85	3.25	76.67	–	–	–	–	9	–
Borehole 536, ore interval 580.0–581.5 m														
C	0.037	0.28	–	99.50	45.07	17.60	–	62.67	–	–	–	17	18	–
N-C	0.053	0.32	–	99.46	26.07	9.42	–	35.49	–	–	45	8	–	–
C	0.034	1.82	–	99.72	33.15	21.24	–	54.39	–	–	–	13	19	4

Note: See Table 1. Additional components: SO₃ 2.76 (sample 55) and 7.68 (sample 53); Fe_{py} 2.27 (sample 24); S_{py} 2.60 (sample 24). The total carbonate includes FeCO₃ 2.64 (sample 74), 1.95 (sample 72), and 1.43 (sample 70). Glauconite and hausmannite are present in samples 39 and 37.

and replaced by carbonates and cut by carbonate veinlets that testify to a later origination of carbonate as compared to oxide segregations. The carbonate material is represented by rhodochrosite with a calcite or manganocalcite admixture.

All varieties of carbonates were picked out from the samples studied. It should be noted that the recognition of the five aforementioned groups is somewhat a matter of convention because the carbonate materials are closely interrelated and it is virtually impossible to select a pure specific material for isotopic study. Although the samples were carefully picked out under the binocular microscope, their major part contains only 80–90% of the respective carbonate material.

Carbonates from all five groups were observed at both the Chiatura and Kvirila deposits. Because the number of samples from the Kvirila deposit was restricted and carbonates of groups II–V are believed to be genetically similar at both deposits, we separated the ores from the Kvirila deposit into only two groups. The first of them corresponds to the first group from the Chiatura deposit, and the second one unites groups II–V from this deposit.

At the Chiatura deposit, the samples for isotopic study of manganese carbonate ore were collected from open pits, adits and boreholes at nine sites in the central part of the deposit within the Darkveti and Itkhvisi highlands (Fig. 1). At the Kvirila deposits, the samples were taken from the cores of boreholes, which were drilled at the Rodinauli and Cholaburi sites in 1982. They are also situated in the central part of the deposit. Samples were taken throughout the entire ore stratum—from subore sand to supraore spongolitic sandstone (Fig. 2).

THE TECHNIQUE OF SAMPLE PREPARATION FOR ISOTOPE ANALYSIS

The release of CO_2 from manganese carbonate ore for isotope analysis was performed following the well-known method of stepwise carbonate breakdown in the water-free orthophosphoric acid (H_3PO_4) in vacuum. The application of this method is caused by the fact that natural carbonate rocks are mostly represented by a mechanical mixture of different minerals. These minerals are frequently out of isotopic equilibrium and may be related to distinct stages of carbonate formation. For example, the later catagenic carbonates may occur along with diagenic minerals. Our experience shows that in complicated natural objects such as sedimentary carbonate rocks, the isotopic composition of calcite and coexisting carbonate minerals, poorly soluble in acid, should be studied separately.

The sample breakdown was conducted in two stages as follows. A finely ground sample was first decomposed in orthophosphoric acid at the room temperature during an hour following the routine method (McCrea, 1950). It was assumed that the released CO_2 is related

to the product of calcite dissolution (Walters *et al.*, 1972). Then the supplementary breakdown of the sample was carried out at 100°C during 1.5 h by means of reactor immersion in a vessel with a boiling water. The released CO_2 corresponds to the product of poorly soluble carbonate decomposition (Rosenbaum and Shepard, 1986). In our case, these are minerals of the manganocalcite–rhodochrosite isomorphic series.

Mass-spectrometer measurements were performed with the mass-spectrometer MI-1201V. The reproducibility of parallel runs was not worse than $\pm 0.25\%$.

RESULTS OF ISOTOPE STUDIES

Carbon and oxygen. All isotope data obtained for various types of carbonate rocks from the deposits under study are given in Tables 3 and 4 and shown in master plots (Figs. 4 and 5). As is evident, the isotopic composition of carbon and oxygen varies rather widely. The widest range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is characteristic of carbonate material from the Chiatura deposit. Variation limits for manganese carbonates are $-(34.5-8.3\%)$ and $18.9-30.5\%$, respectively. Variations for specific groups are as follows ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively in ‰): group I (gray cryptocrystalline carbonate material)— -24.7 to -9.0 and 24.1 to 28.5 ; group II (altered carbonate material)— -33.3 to -8.6 and 22.3 to 28.8 ; group III (carbonate ooids)— -35.4 to -9.5 and 19.1 to 30.5 ; group IV (veined carbonate)— -31.9 to -12.4 and 19.3 to 28.8 ; group V (carbonate cement in oxide-carbonate ore)— -20.6 to -7.1 and 18.0 to 28.7 .

As is evident from these data, the least variations of isotopic composition are attributed to the least altered carbonate material (group I), and the greatest fluctuations are related to the carbonate material from ooids (group III) and veinlets (group IV). In general, the ore from the Chiatura deposit does not reveal a systematic correlation $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$, although these values extend from the left lower corner toward the right upper corner of the plot for the cement carbonate (Fig. 4, field 5). This may testify to the mixing of different sources of carbonate materials, distinct in isotopic composition.

Attention should be drawn to the lack of substantial difference in oxygen isotopic composition of various groups of carbonate materials from manganese ore. If different types of carbonate material would have formed under distinct conditions and there would have been distinct CO_2 sources, this would inevitably be reflected in the isotopic composition of carbon and oxygen.

Nevertheless, substantial differences between rock groups in oxygen isotopic composition were not found (see communication 2 for details). In general, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and their distributions in different groups are very close to each other; at the same time, there are some specific isotopic features attributed to a certain group. For example, most $\delta^{18}\text{O}$ determinations for almost all rocks fall in the range $26-28\%$. It is believed

Table 3. Carbon and oxygen isotopic compositions of carbonate materials from manganese ore, Chiatura deposit

Analysis no.	Sample no.	Sample composition and location	Calcite		Rhodochrosite	
			$\delta^{13}\text{C}$, ‰ (PDB)	$\delta^{18}\text{O}$, ‰ (SMOW)	$\delta^{13}\text{C}$, ‰ (PDB)	$\delta^{18}\text{O}$, ‰ (SMOW)
		I. Dark gray cryptocrystalline carbonate from the opal-carbonate groundmass				
2652	20	Darkveti Highland, site 4, open pit 1987	—	—	—9.8	28.1
2645	19	<i>Ibid.</i>	—	—	—16.3	26.8
2655	26	"	—	—	—7.7	26.0
1717	1875	<i>Ibid.</i> , open pit, 1983	—	—	—25.7	26.3
1720	1879	<i>Ibid.</i>	—	—	—16.6	27.1
2641	108	<i>Ibid.</i> , site 8, open pit, 1982	—	—	—24.7	26.2
2689	1059	<i>Ibid.</i> , site 4, open pit 5, 1987	—18.8	24.1	—13.8	26.4
2688	1057	<i>Ibid.</i>	—	—	—15.5	26.6
2684	1047	"	—	—	—9.0	26.7
2764	1117	<i>Ibid.</i> , site 10, open pit, 1987	—11.2	26.9	—12.3	26.3
2765	1123	<i>Ibid.</i> , site 10, borehole 830	—	—	—12.2	28.5
2766	1126	<i>Ibid.</i>	—	—	—10.2	27.0
2768	1130	<i>Ibid.</i> , borehole 828	—19.9	28.6	—15.3	28.3
2770	1136	<i>Ibid.</i> , borehole 826	—9.6	28.9	—9.6	28.1
2661	144	Akhali-Itkhvisi Highland, adit, 1982	—	—	—9.6	27.2
2665	145	<i>Ibid.</i>	—10.7	28.6	—11.5	27.8
2668	146	"	—	—	—9.1	27.8
2670	147	"	—10.7	27.9	—11.4	27.4
2677	152	"	—	—	—10.2	27.4
		II. Light gray loose, often crystalline carbonate				
2653	20	Darkveti Highland, site 4, open pit 1982	—	—	—14.5	28.2
2643	17	<i>Ibid.</i>	—	—	—20.3	26.4
2646	18	"	—	—	—18.4	25.9
2648	24	"	—	—	—33.3	27.3
1731	1888	<i>Ibid.</i> , open pit, 1983	—	—	—13.3	21.1
1733	1889	<i>Ibid.</i>	—	—	—16.5	20.6
2649	31	<i>Ibid.</i> , site 8, open pit, 1982	—20.5	27.2	—18.6	28.2
2640	109	<i>Ibid.</i>	—17.9	23.0	—17.2	26.2
2642	108	"	—	—	—31.6	26.3
2695	1076	<i>Ibid.</i> , site 4, open pit, 1987	—23.0	22.3	—18.9	23.4
2763	1056	<i>Ibid.</i>	—	—	—18.7	25.2
2685	1047	"	—15.4	22.3	—8.9	26.2
2700	1093	<i>Ibid.</i> , site 3, adit, 1987	—17.2	24.5	15.6	25.7
2771	1136	<i>Ibid.</i> , borehole 826	—13.0	23.7	—10.9	28.0
2773	1141	<i>Ibid.</i> , borehole 827	—15.2	22.1	—15.7	24.0
2664	144	Akhali-Itkhvisi Highland, adit, 1982	—	—	16.9	27.8
2666	145	<i>Ibid.</i>	—14.8	28.1	—15.8	27.9
2669	146	"	—	—	—14.1	27.5
2672	147	"	—13.6	25.9	—16.3	27.6
2673	148	"	—17.7	25.4	—17.5	27.4
2674	149	"	—	—	—13.8	27.9
2675	150	"	—	—	—10.3	27.3
2676	152	"	—	—	—8.6	27.9
2679	153	"	—	—	—8.9	27.4
2680	154	"	—	—	—9.7	27.5
2681	155	"	—	—	—10.3	27.6
2682	156	"	—	—	—9.0	27.8

Table 3. (Contd.)

Analysis no.	Sample no.	Sample composition and location	Calcite		Rhodochrosite	
			$\delta^{13}\text{C}$, ‰ (PDB)	$\delta^{18}\text{O}$, ‰ (SMOW)	$\delta^{13}\text{C}$, ‰ (PDB)	$\delta^{18}\text{O}$, ‰ (SMOW)
		III. Carbonate ooids				
2654	20	Darkveti Highland, site 4, open pit, 1982	—	—	—17.0	25.8
2657	26	<i>Ibid.</i>	—	—	—10.6	22.0
2706	1109	"	—	—	—35.4	27.0
2774	1143	"	—10.8	19.6	—9.5	18.9
1701	1870	<i>Ibid.</i> , open pit, 1983	—20.7	20.2	—	—
1703	1871	<i>Ibid.</i>	—	—	—20.4	28.4
1708	1872	"	—	—	—15.6	26.8
1711	1873	"	—	—	—17.0	24.1
1739	1893	"	—	—	—17.7	26.1
1744	1896	"	—	—	—11.8	27.0
1781*	1900	<i>Ibid.</i> , site 8	—	—	—14.0	29.7
1782*	1901	<i>Ibid.</i>	—	—	—12.8	30.5
2772	1136	<i>Ibid.</i> , borehole 826	—14.5	19.1	—11.6	26.4
2767	1126	<i>Ibid.</i> , borehole 830	—25.7	20.1	—24.0	21.0
2662	144	Akhali-Itkhvisi Highland, adit, 1982	—15.1	28.8	—16.7	27.4
2667	145	<i>Ibid.</i>	—15.7	28.3	—16.3	28.0
2672	147	"	—14.2	27.0	—15.7	27.2
		IV. Light gray carbonate from veinlets				
2644	17	Darkveti Highland, site 4, open pit 1982	—30.0	27.5	—31.9	26.3
2647	24	<i>Ibid.</i>	—19.5	27.0	—31.1	26.5
2692	1068	<i>Ibid.</i> , open pit, 1987	—21.8	25.6	—23.0	26.3
2690	1059	<i>Ibid.</i>	—21.8	20.0	—20.5	19.3
2691	1063	"	—16.9	25.1	—12.9	26.3
2650	31	"	—19.5	28.7	—21.4	28.9
2701	1093	<i>Ibid.</i> , site 3, adit, 1987	—	—	—16.1	25.3
2707	1109	<i>Ibid.</i> , site 9, adit, 1987	—17.3	25.4	—18.6	25.3
2769	1130	<i>Ibid.</i> , borehole 828	—18.7	28.6	—12.4	27.5
2775	1146	<i>Ibid.</i> , borehole 832	—19.0	26.6	—	—
		V. Carbonate from the oxide ore cement				
2660	23	Darkveti Highland, site 4, open pit, 1982	—	—	—20.6	23.4
1721	1880	<i>Ibid.</i> , open pit, 1983	—17.4	18.8	—	—
1734	1890‡	<i>Ibid.</i>	—16.5	17.5	—	—
1735	1890	"	—16.3	18.5	—	—
1736	1891	"	—17.3	23.0	—	—
1738*	1892	"	—	—	—16.7	21.4
1740*	1894	"	—	—	—19.1	22.0
2658	27‡	<i>Ibid.</i> , site 8, open pit, 1982	—11.2	27.3	—16.1	24.8
2659	28	<i>Ibid.</i>	—	—	—9.6	26.6
2678	153	Akhali-Itkhvisi Highland, adit, 1982	—	—	—9.3	27.1
2697	1083	<i>Ibid.</i>	—	—	—8.3	26.5

Note: The dash denotes the absence of mineral or the lack of data.

Table 4. Carbon and oxygen isotopic compositions of carbonate materials from manganese ore, Kvirila deposit

Ana- lysis no.	Sample no.	Sample composition and location (borehole no. and depth in meters)	Calcite		Rhodochrosite	
			$\delta^{13}\text{C}$, ‰ (PDB)	$\delta^{18}\text{O}$, ‰ (SMOW)	$\delta^{13}\text{C}$, ‰ (PDB)	$\delta^{18}\text{O}$, ‰ (SMOW)
I. Gray cryptocrystalline carbonate						
		Rodinauli site				
3485	74-1	518, 576.10 m	—	—	−14.1	25.8
3491	87-1	536, 580.80 m	—	—	−11.5	28.7
3489	84-1	581.45 m	−15.0	24.6	−18.7	26.3
3488	81-1	808, 560.80 m	−12.9	29.3	−14.0	28.6
3463	26-1	824, 607.60 m	—	—	−13.1	24.9
2461	25-1	607.70 m	—	—	−17.1	26.3
		Cholaburi site				
3479	64-1	868, 576.80 m	−8.0	29.8	−11.0	27.8
3478	63-2	577.00 m	−7.3	27.6	−19.2	25.4
3466	34-2	889, 587.3 m	—	—	−13.1	26.3
II. White and pink crystalline carbonate						
		Rodinauli site				
3486	74-2	518, 576.1 m	−0.5	24.9	−10.7	25.4
3484	72-2	576.3 m	—	—	−7.5	27.1
3483	70-2	576.7 m	—	—	−3.7	22.2
3482	69-2	577.0 m	—	—	−4.2	21.1
3490	85-2	536, 581.3 m	—	—	−3.6	23.0
3484	79-2	808, 561.3 m	—	—	−6.6	23.8
3473	54	814, 549.2 m	−6.7	22.7	−6.6	28.1
3499	53	549.3 m	—	—	−7.2	22.2
3472	51-2	549.4 m	−7.1	23.6	−7.2	26.6
3471	49-2	550.3 m	—	—	−5.6	28.3
3464	27-2	824, 607.4 m	—	—	−5.4	29.8
3492	27-1	607.4 m	—	—	−4.9	28.4
3462	25-2	607.7 m	−3.7	23.8	−5.6	22.2
		Cholaburi site				
3481	65	868, 576.5 m	—	—	−3.3	27.0
3480	64-2	576.8 m	−0.9	24.8	−3.7	27.6
3476	61-2	577.4 m	—	—	−5.4	26.1
3475	60-2	577.5 m	—	—	−2.3	27.5
3474	59-2	577.65 m	—	—	−8.1	28.1
3469	44-2	889, 585.0 m	—	—	−8.4	24.9
3456	34-1	587.3 m	—	—	−4.2	23.9

Note: See Table 3.

that respective carbonates from all groups were formed under common conditions and were related to one source of carbon dioxide solutions. Samples with lower $\delta^{18}\text{O}$ indicate distinct physicochemical conditions and

other sources of ore-forming solutions, which are characterized by a lower $\delta^{18}\text{O}$.

The carbon isotopic composition also testifies to the isotopically inhomogeneous CO_2 reservoir or to the

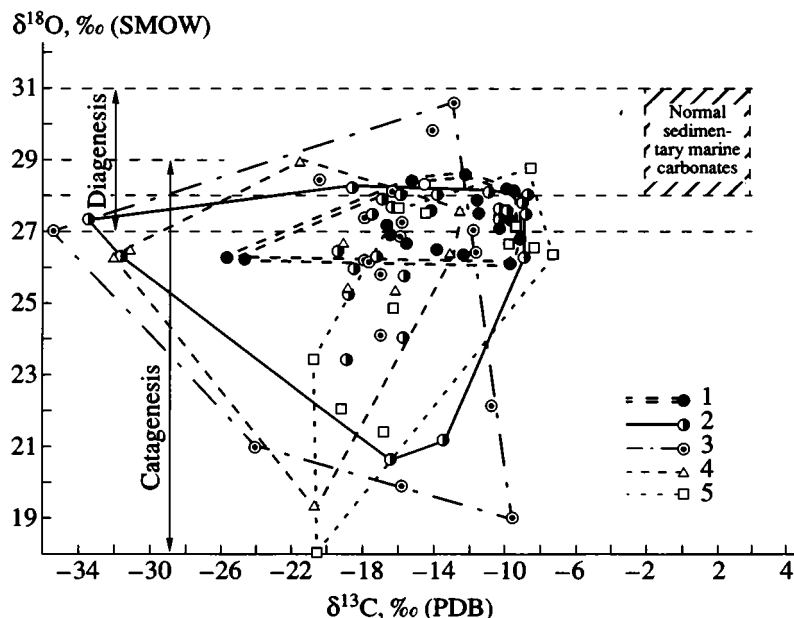


Fig. 4. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonate materials from manganese ore at the Chiatura deposit. (1) Dark gray to black cryptocrystalline material from opal-carbonate groundmass; (2) light gray to white loose porous, often crystalline material; (3) white and pink material from rounded inclusions (ooids); (4) light gray and white coarse-crystalline material from veinlets; (5) gray and pink coarse-spherulitic material from the oxide-carbonate ore cement.

existence of several sources that supplied the carbon dioxide to manganese ore carbonates.

The carbonate ore from the Kvirila deposit is characterized by a narrower range of C and O isotopic composition as compared with the Chiatura ore. In the least

altered carbonate material (group I), $\delta^{13}\text{C}$ varies from -19.2 to -7.3‰ and $\delta^{18}\text{O}$ —from 24.6 to 29.8‰ and are close to those for the carbonate material (group I) from the Chiatura deposit. For the later, altered carbonate material (group II) these values vary from -10.7 to -2.3‰ and from 21.1 to 29.8‰ , respectively.

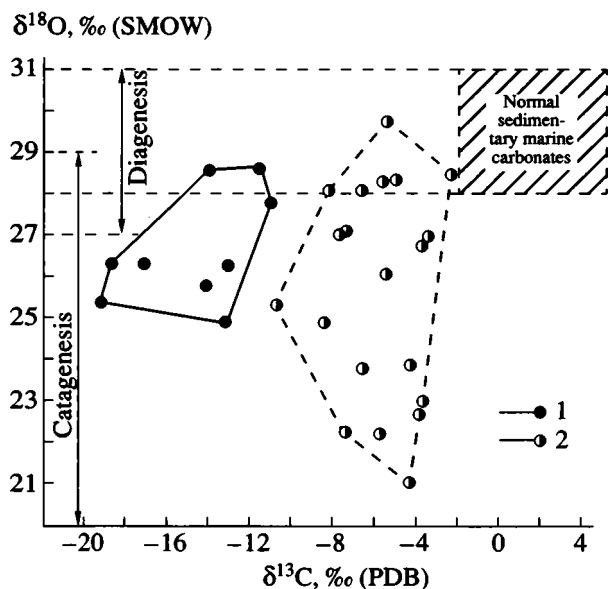


Fig. 5. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonate materials from Mn ore at the Kvirila deposit. (1) Dark gray to black cryptocrystalline material from opal-carbonate groundmass; (2) light gray to white and pinkish white spherulitic material.

The aforementioned groups occupy separated fields on the plot $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ (Fig. 5). Light crystalline varieties of the group II are characterized by a heavier carbon and by a wider range of $\delta^{18}\text{O}$. As in rocks from the Chiatura deposit, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ reveal a nonuniform distribution within certain groups (see communication 2 for details) indicating a heterogeneous source and specific formation conditions of rocks related to one or other group.

The crystalline light manganese carbonate ore (group II) from the Kvirila deposit is characterized by the heaviest carbon and has not isotope counterparts among the ore from the Chiatura deposit. This may testify to some important differences in the sources of material (ore material, CO_2 , solutions, etc.) and formation conditions of deposits under comparison.

As a rule, the isotopic composition of calcite from the rocks and ore of the Chiatura deposit is close to that of coexisting manganese carbonates. This indicates their isotopic equilibrium or a state approaching it. However, some samples of calcite are noticeably distinct in isotopic composition of carbon (up to 11.6‰ , analysis 2647) and oxygen (up to 7.34‰ , analysis 2772) toward both lower and higher values (Table 5).

Table 5. Sulfur isotopic composition of sulfides and sulfates from manganese ore at the Chiatura and Kvirila deposits

Analysis no.	Sample no.	Sample composition and location	$\delta^{34}\text{S}$, ‰
Chiatura deposit			
I. Pyrite from carbonate ore			
2743	144	Akhali-Itkhvisi Highland, adit, 1987	10.6
2745	1047	Darkveti Highland, site 4, open pit 5, 1987	-15.0
2746	1052	<i>Ibid.</i>	-17.2
2749	1076	"	9.8
1700	1970c	<i>Ibid.</i> , open pit, 1983	4.5
1704	1871c	<i>Ibid.</i>	23.3
1707	1872c	"	4.4
1715	1874b	"	-6.8
1718	1877	"	-19.0
1719	1878	<i>Ibid.</i> , carbonatized sandstone	-16.0
2755	1107	<i>Ibid.</i> , site 9, adit, 1987	7.2
2757	1109	<i>Ibid.</i>	2.0
2761	1141	<i>Ibid.</i> , borehole 827, 22.5 m	-10.9
II. Secondary barite from cavities in carbonate-oxide ore			
2741	23	Darkveti Highland, site 4, open pit, 1982	3.0
2747	1056	<i>Ibid.</i> , site 4, open pit 5, 1987	41.2
2750	1076	<i>Ibid.</i>	24.2
2742	27a	<i>Ibid.</i> , site 8, open pit, 1982	-4.9
2756	1107	<i>Ibid.</i> , site 9, adit, 1987	24.0
III. Secondary gypsum			
2758	1117	Darkveti Highland, site 10, open pit, 1987	2.5
2760	1145	<i>Ibid.</i> , borehole 832, 120.7 m	7.9
Kvirila deposit			
1659	1857b	Borehole 508, 570.45 m. Pyrite from the manganese carbonate ore	38.2
1680	1863b	Borehole 549, 583.45 m. Pyrite from manganese oxide ore	-20.3
1692	1867c	Borehole 1022, 425.2 m. Pyrite from oolitic manganese ore	17.8

Available data for the Chiatura deposit do not allow us to establish any definite regularity in the distribution of these deviations. However, many calcites tend to be enriched in light C and O isotopes relative to coexisting manganese carbonates.

For rocks of the Kvirila deposit, such a tendency was not noted (Table 5). Calcites differ in isotopic composition of the carbon only, the oxygen only, or both carbon and oxygen toward either lighter or heavier values. Hence, a considerable part of the calcites is of later origin, and they were formed at a distinct temperature from carbon dioxide solutions bearing specific isotopic characteristics.

Sulfur. The isotopic composition of sulfur was studied in sulfides (pyrite) and sulfates (barite, gypsum) from the Chiatura and Kvirila deposits. Results of isotope analyses are given in Table 5. The $\delta^{34}\text{S}$ variation is rather wide, and for the rocks from the Chiatura deposit ranges from -19.0 to 41.2‰. Pyrites from this deposit

have been studied most thoroughly. $\delta^{34}\text{S}$ in pyrite varies from -19.0 to 23.3‰, in barite—from -4.9 to 41.2‰, in gypsum (2 samples)—from 2.5 to 7.9‰.

A rather uniform distribution of $\delta^{34}\text{S}$ throughout the entire range calls our attention.

Experimental points are more frequent within the -20 to -14‰ and 4-12‰ intervals. It should be noted that the studied collection does not contain samples with zero $\delta^{34}\text{S}$ values.

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REFERENCES

Avaliani, G.A., *Margantsevy mestorozhdeniya Gruzii (geologiya, mineralogiya, genezis)* (Manganese Deposits of

- Georgia: Geology, Mineralogy, and Genesis), Moscow: Nauka, 1982.
- Betekhtin, A.G., *Promyshlennyye margantsevye rudy SSSR* (Economic Manganese Ores of the USSR), Moscow: Akad. Nauk SSSR, 1946.
- Butuzova, G.Yu., Study of Zeolites from the Heulandite Group: Zeolite from Paleogene Deposits of the Southern USSR, *Litol. Polezn. Iskop.*, 1964, no. 4, pp. 66–79.
- Chiaturestoe mestorozhdenie margantsa* (The Chiatura Manganese Deposit), Moscow: Nedra, 1964.
- Dolidze, D.P., Machabeli, G.A., Tabagari, V.I., and Gogvadze, B.S., Lithogenesis of Oligocene Mn-bearing Deposits of the Kvirila Depression and Further Development of Prospecting and Exploration, in *Novye dannye po margantsevyim mestorozhdeniyam SSSR* (New Data on Manganese Deposits of the USSR), Moscow: Nauka, 1980, pp. 75–86.
- Dvorov, V.I. and Sokolova, E.A., Geological and Geochemical Prerequisites for the Formation of Manganese ore at the Mangyshlak Deposit: Communication 2. Elisional Epigenetic Model of Manganese ore Formation, *Litol. Polezn. Iskop.*, 1987, no. 4, pp. 28–41.
- Dzotsenidze, G.S., Genesis of the Chiatura Manganese Deposit, *Litol. Polezn. Iskop.*, 1965, no. 1, pp. 3–17.
- Dzotsenidze, G.S., Geological Formation Conditions of Manganese Deposits of Chiatura and Kvirila Depression, in *Novye dannye po margantsevyim mestorozhdeniyam SSSR* (New Data on Manganese Deposits of the USSR), Moscow: Nauka, 1980, pp. 62–69.
- Edilashvili, V.Ya., Lekvinadze, R.D., and Gogiberidze, V.V., Effect of Tectonics on the Manganese Deposition in Georgia, *Sov. Geol.*, 1973a, no. 4, pp. 106–114.
- Edilashvili, V.Ya., Lekvinadze, R.D., Gogiberidze, V.V., and Burdzhnashvili, D.S., Geological Conditions of Manganese Deposition in Georgia, in *Materialy Kavkaz. Inst. Miner. Syr'ya* (Materials of Caucasus Inst. Mineral Resources), 1973b, Ser. Geol., vol. 10(12), pp. 135–142.
- Gogishvili, V.G., Gogishvili, T.Sh., Zuliashvili, T.G., and Chkheidze, R.G., Silica-rich Zeolites from the Transcaucasia, in *Voprosy geologii i tekhnologii poleznykh iskopayemykh Kavkaza* (Problems of Geology and Technology of Mineral Resources of the Caucasus), Tbilisi: Sabchota Sakartvelo, 1979, pp. 115–121.
- Gogishvili, V.G., Khamkhadze, N.I., and Guniava, V.I., Manganese Ore Belt of the Transcaucasia, in *Novye dannye po margantsevyim mestorozhdeniyam SSSR* (New Data on Manganese Deposits of the USSR), Moscow: Nauka, 1980, pp. 117–126.
- Gogishvili, V.G., Khamkhadze, N.I., and Guniava, V.I., Genetic Types of Siliceous–Manganese Mn Mineralization in the Transcaucasia, in *Geologiya i geokhimiya margantsa* (Geology and Geochemistry of Manganese), Moscow: Nauka, 1982, pp. 140–147.
- Khamkhadze, N.I., Relationships between Silica and Ore Deposition at Manganese Deposits of the Georgia, in *Vulkanizm i litogenez* (Volcanism and Lithogenesis), Tbilisi: Metsniereba, 1981, pp. 141–146.
- Khamkhadze, N.I., Tectonic and Hydrothermal Reactivation of Siliceous–Manganese Mn Deposition Areas of Georgia in Oligocene, in *Usloviya obrazovaniya rudnykh mestorozhdenii* (Formation Conditions of Ore Deposits), Moscow: Nauka, 1986, pp. 834–838.
- Khamkhadze, N.I. and Tumanishvili, G.P., *Paleotectonic Conditions of Manganese Ore Localization in the Kvirila Depression* (Manganese Ore Formation in the USSR Territory), Moscow: Nauka, 1984, pp. 227–235.
- Kholodov, V.N., New Insight in the Knowledge of Catagenesis: Communication 1, *Litol. Polezn. Iskop.*, 1982a, no. 3, pp. 3–22.
- Kholodov, V.N., New Insight in the Knowledge of Catagenesis: Communication 2, *Litol. Polezn. Iskop.*, 1982b, no. 5, pp. 15–32.
- Laliev, A.G., *Maikopskaya seriya Gruzii* (Maikop Group in the Georgia), Moscow: Nedra, 1964.
- Lekvinadze, R.D., Edilashvili, V.Ya., and Khuchua, M.F., Geological Formation Conditions of Manganese Rocks in the Georgia, in *Margantsevyim mestorozhdeniyam SSSR* (Manganese Deposits of the USSR), Moscow: Nauka, 1967, pp. 214–224.
- Machabeli, G.A., Specific Features of Sedimentation and Diagenesis of Oligocene Mn-bearing Deposits of the Georgia, in *Usloviya obrazovaniya rudnykh mestorozhdenii* (Formation Conditions of Ore Deposits), Moscow: Nauka, 1986, vol. 2, pp. 839–849.
- Machabeli, G.A. and Khamkhadze, N.I., Lithological Features of Oligocene Mn-bearing Deposits of the Caucasus and a Source of Manganese, in *Voprosy geologii i tekhnologii poleznykh iskopayemykh Kavkaza* (Problems of Geology and Technology of Mineral Resources of the Caucasus), Tbilisi: Sabchota Sakartvelo, 1979, pp. 33–39.
- Makharadze, A.I., Sources and Supply of Mn, Si, Fe, and P into Lower Oligocene Sediments of the Western Georgia, *Dokl. Akad. Nauk SSSR*, 1972, vol. 202, no. 4, pp. 929–931.
- Makharadze, A.I., Siliceous Zeolite Rocks from the Maikop Group of Georgia and Their Formation Conditions, in *Materialy po poleznyim iskopayemyim Kavkaza* (Materials on Mineral Resources of the Caucasus), Tbilisi: Sabchota Sakartvelo, 1979, pp. 207–218.
- Makharadze, A.I. and Chkheidze, R.G., Lithology of Oligocene Deposits of the Kvirila Depression and the Genesis of Related Mineral Resources, *Trudy KIMS*, 1971, vol. 9 (2), pp. 177–188.
- McCrea, J.M., On the Isotopic Chemistry of Carbonates and a Paleotemperature Scale, *J. Chem. Phys.*, 1950, vol. 18, no. 6, pp. 849–857.
- Merabishvili, M.S., Chkheidze, R.G., Dolendzhishvili, Ts.G., Begiashvili, T.N., and Khachaturyan, K.K., Silica-rich Zeolites of the Transcaucasia and Their Possible Usage, in *Voprosy geologii i tekhnologii poleznykh iskopayemykh Kavkaza* (Problems of Geology and Technology of Mineral Resources of the Caucasus), Tbilisi: Sabchota Sakartvelo, 1979, pp. 221–230.
- Mstislavskii, M.M., Do "Classic Sedimentary" Manganese Deposits of the Chiatura Type Actually Exist in Nature? *Geol. Rudn. Mestorozhd.*, 1985, vol. 27, no. 6, pp. 3–16.
- Mstislavskii, M.M., Genesis of Oligocene Manganese Ore Deposits in the Southern USSR. Reply to the Paper "Sedimentary or Hydrothermal Sedimentary Manganese Deposits of the Chiatura Type?" by L.E. Shterenberg (*Izv. Akad. Nauk SSSR, Ser. Geol.*, 1988, no. 2), *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1989, no. 8, pp. 131–143.
- Paragenesis metallov i nefii v osadochnykh tolshchakh neftegazonosnykh basseinov* (Paragenesis of Metals and Oil in Sedimentary Sequences of Oil- and Gas-bearing Depressions), Gorzhvskii, D.I., Kartsev, A.A., Pavlov, D.I., et al., Eds., Moscow: Nedra, 1990.

- Pavlov, D.I., Link between Sedimentary Manganese Iron and Deposits and Oil- and Gas-bearing Depressions, *Geol. Rudn. Mestorozhd.*, 1989, vol. 31, no. 2, pp. 80–91.
- Pavlov, D.I. and Dombrovskaya, Zh.V., Sedimentary Manganese Deposits as a Result of Ascending Discharge of Ground Water of Oil- and Gas-bearing Depressions, *Otech. Geol.*, 1993, no. 8, pp. 21–26.
- Rosenbaum, J. and Sheppard, S.M.F., An Isotopic Study of Sediments, Dolomites, and Ankerites at High Temperatures, *Geochim. Cosmochim. Acta*, 1986, vol. 50, pp. 1147–1150.
- Sapozhnikov, D.G., Formation Conditions of Manganese Deposits of the Southern Russian Platform and Crimean–Caucasian Geosyncline, *Geol. Rudn. Mestorozhd.*, 1967, no. 1, pp. 74–87.
- Shterenberg, L.E., Genesis of the Chiatura Manganese Deposit, *Geol. Rudn. Mestorozhd.*, 1985, vol. 27, no. 1, pp. 91–101.
- Shterenberg, L.E., Sedimentary or Hydrothermal Sedimentary Manganese Deposits of the Chiatura Type?, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1988, no. 2, pp. 137–140.
- Strakhov, N.M., Shterenberg, L.E., Kalinenko, V.V., and Tikhomirova, E.S., Geochemistry of Sedimentary Manganese Ore Formation, *Trudy GIN*, 1968, issue 185, p. 495.
- Tabagari, D.V., *Distribution and Composition of Genetic Types of Manganese Ore at the Chiatura Deposit*, Moscow: Nauka, 1980, pp. 86–94.
- Tabagari, D.V., Some Specific Features of Structure and Formation of Ore Lodes at the Chiatura Deposit, in *Margantsevoe rudoobrazovanie na territorii SSSR* (Manganese Ore Formation in the USSR Territory), Moscow: Nauka, 1984, pp. 209–216.
- Tumanishvili, G.P., Lithology and Formation Conditions of Oligocene Mn-bearing Deposits of the Kvirila Depression, Western Georgia, *PhD (Geol.–Miner.) Dissertation*, Rostov-on-Don: Rostov State Univ., 1989.
- Walters, H.I., Claypool, G.E., Jr., and Philip, Ch.W., Reaction Rates and 18-O Acid Preparation Method, *Geochim. Cosmochim. Acta*, 1972, vol. 36, no. 2, pp. 129–140.

Copper Behavior in the Aluminosilicate Phases at Oxidizing Conditions: Evidence from Experimental Data

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Abstract—The behavior of copper traces in glasses and glass-ceramics (partially crystallized glasses), which are synthesized analogs of the major volcanogenic rocks and in natural sulfide-bearing dacites at change of temperature and redox conditions were experimentally modeled. Modes of occurrence and mobilization specifics of Cu were studied. Thermodynamic analysis of alteration processes, oxidation, and redistribution of Cu in the studied aluminosilicate phases was carried out. The experimental results with geochemical data on volcanogenic rocks in the vicinity of pyritic copper deposits were compared. It was found that the increase of temperature and oxygen potential, which are typical of surface conditions, results in the considerable increase of the ore-generating ability of the igneous rocks with respect to Cu and produces metal-bearing solutions.

Many world copper deposits are confined to different volcanogenic rocks that underwent change of temperature and oxidizing conditions at postmagmatic stage. To evaluate the copper potential of these rocks, conditions of its concentration and mobilization in the volcanogenic rocks, we experimentally studied the modes of occurrence and migration of copper traces in the aluminosilicate systems at change of physicochemical parameters (temperature and oxygen).

Based upon the obtained experimental data, we carried out a thermodynamic analysis of the copper redistribution at redox equilibria in the aluminosilicate phases.

Earlier, it was discovered that, upon heating of air, copper is redistributed and concentrates at the surface of plates and grains of $\text{Cu}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$ glass (Kamiya *et al.*, 1986), as well as in aluminosilicate phases of the granite eutectic with copper traces (Durasova *et al.*, 1989). Therefore, it was expedient to experimentally study the behavior copper traces in glasses and glass-ceramics (analogs of the major igneous rocks), as well as in volcanogenic rocks (dacites), whose altered varieties are widespread within pyritic

copper deposits (Karpukhina and Baranov, 1995). Evidently, the copper redistribution and concentration, observed in simple glasses, may occur in natural volcanogenic rocks upon heating at oxidized conditions (Durasova *et al.*, 1994).

According to data reported by (Gandella and Holland, 1984) and our publications on the mode of copper occurrence in the Fe-free aluminosilicate systems, which were synthesized at an oxygen potential typical of several natural processes and close to f_{O_2} of Ni–NiO buffer (Durasova *et al.*, 1987), copper mainly occurs in low-oxidized state. Evidently, this type of mode of copper occurrence in magmatic phases might largely control its behavior upon subsequent heating under high oxygen potentials.

EXPERIMENTAL AND ANALYTICAL PROCEDURES

We synthesized the Cu-bearing aluminosilicate phases of the rhyolitic, andesitic, and basaltic composition in the evacuated quartz ampoules with the Ni–NiO buffer at a temperature of 900–1300°C. Experiment

Table 1. Chemical composition of the synthesized glasses and ceramics

Systems		Oxides, wt %								Minerals
		SiO ₂	TiO ₂	Al ₂ O ₃	FeO/CoO	MgO	CaO	Na ₂ O	K ₂ O	
Rhyolite	Granite, after Daly 900–1000°C	70.2	0.4	14.5	3.2	0.9	2.0	3.5	4.1	Quartz
	Granite eutectic 1500°C	79.6	–	11.7	–	–	–	4.1	4.6	no
Andesite	1100–1300°C	54.0	1.4	17.0	7.7	6.9	8.0	3.0	1.1	Pyroxene
Basalt	Hawaiite 1000–1200°C	49.5	2.9	16.6	12.7	3.9	7.5	5.0	1.2	Pyroxene plagioclase
	Boninite 1350–1380°C	54.2	0.5	10.1	7.7	16.2	8.6	1.2	0.5	Ilmenite

Table 2. Copper extraction by HCl solution from aluminosilicate glasses, glass-ceramics, and sulfide-bearing volcanogenic rocks

Sample no.	Rock	Synthesis condition	CuO content in samples, wt %	Heating conditions	Glass weight, mg	Volume of solution, ml	Cu content in the solution after 40-min contact with grains, (1)/ml	Cu extraction from glasses by 5N HCl, %
232-1	Basaltic hawaiite	1200°C, 6 h, f_{O_2} Ni-NiO	0.44	Without heating	48.6	2	<0.2	<0.02
232-1-500	"	"	"	500°C, 10 days, air f_{O_2}	39.2	2	74.6	87.00
232-2	"	1100°C, 24 h, f_{O_2} Ni-NiO	"	Without heating	47.0	2	0.4	0.40
232-2-500	"	"	"	500°C, 10 days, air f_{O_2}	46.9	2	89.8	87.0
232-3	"	1100°C, 58 h, f_{O_2} Ni-NiO	"	Without heating	40.0	2	3.6	4.0
232-3-500	"	"	"	500°C, 10 days, air f_{O_2}	42.0	2	73.0	77.0
243-3	"	1200°C, 24 h, f_{O_2} Ni-NiO	0.44	Without heating	40.0	2	4.9	7.0
243-500	"	"	"	500°C, 10 days, air f_{O_2}	40.0	2	70.6	80.0
229-2	Basaltic boninite	1380°C, 6 h, f_{O_2} Ni-NiO	0.31	Without heating	40.3	2	<0.2	<0.02
229-2-500	"	"	"	500°C, 10 days, air f_{O_2}	41.0	2	26.6	48.0
227-5	Andesite	1300°C, 6 h, f_{O_2} Ni-NiO	0.31	Without heating	42.9	2	<0.2	<0.02
227-5-500	"	"	"	500°C, 10 days, air f_{O_2}	41.8	2	69.0	97.0
227-3	"	1200°C, 24 h, f_{O_2} Ni-NiO	"	Without heating	39.9	2	<0.2	<0.02
227-3-500	"	"	"	500°C, 10 days, air f_{O_2}	37.4	2	38.0	69.0
227-1	"	1100°C, 62 h, f_{O_2} Ni-NiO	"	Without heating	39.4	2	<0.2	<0.03
227-1-500	"	"	"	500°C, 10 days, air f_{O_2}	36.7	2	41.0	83.0
242	"	1300°C, 6 h, f_{O_2} Ni-NiO	0.35	Without heating	40.0	2	<0.2	<0.30
242-500	"	"	"	500°C, 10 days, air f_{O_2}	40.0	2	58.8	83.0
215	Rhyolite granitic eutectic	1500°C, 0.5 h, air f_{O_2} (2)	0.35	Without heating	47.4	2	2.6	11.7
215-500	"	"	"	500°C, 10 days, air f_{O_2}	42.7	2	18.9	31.1
233-1	Granitoid granite, after Daly	1000°C, 12 h, f_{O_2} Ni-NiO	0.34	Without heating	56.1	2	2.4	2.1
233-1-500	"	"	"	500°C, 10 days, air f_{O_2}	40.6	2	9.2	29.0
233-3	"	900°C, 58 h, f_{O_2} Ni-NiO	"	Without heating	52.5	2	3.6	11.7
233-3-500	"	"	"	500°C, 10 days, air f_{O_2}	40.1	2	34.8	51.0
244	"	1000°C, 6 h, f_{O_2} Ni-NiO	0.33	Without heating	40.0	2	0.14	0.6
244-500	"	"	"	500°C, 10 days, air f_{O_2}	40.0	2	9.4	14.0
B-1	Altered sulfide- bearing dacites (3)	Natural material	0.0022	Without heating	500.0	2	1.35	23.0
B-1-500	"	"	"	500°C, 10 days, air f_{O_2}	500.0	2	4.55	82.0
B-1-sf	Sulfide component	"	0.0180	Without heating	250.0	1	1.40	3.0
B-1-sf-500	"	"	"	500°C, 10 days, air f_{O_2}	250.0	1	19.00	44.0
B-2	Altered sulfide- bearing dacites (3)	"	0.0210	Without heating	500.0	2	0.20	5.0
B-2-500	"	"	"	500°C, 10 days, air f_{O_2}	500.0	2	3.70	71.0
B-2-sf	Sulfide component	"	0.0220	Without heating	250.0	1	1.50	3.0
B-2-sf-500	"	"	"	500°C, 10 days, air f_{O_2}	250.0	1	37.10	68.0

Note: (1) Grain size 0.2–0.5 mm; (2) based upon EPR data, Cu^{+2} is absent owing to instability of monovalent copper compounds at $T > 1500^\circ C$;
 (3) sulfur content in samples B-1 and B-2 0.7–0.1%.

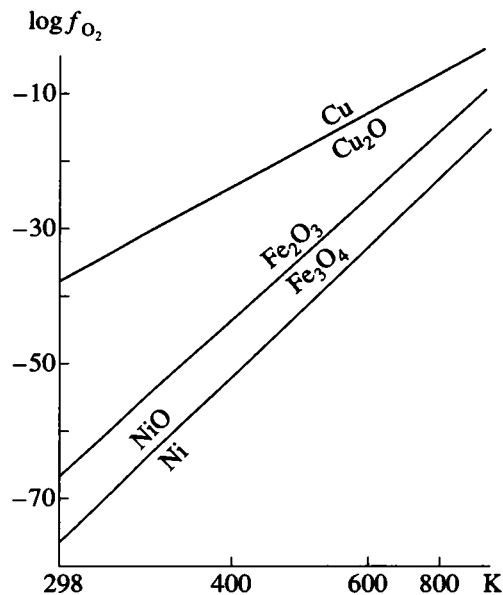


Fig. 1. Oxygen fugacity for metal–oxide and oxide (1)–oxide (2) systems as a function of temperature.

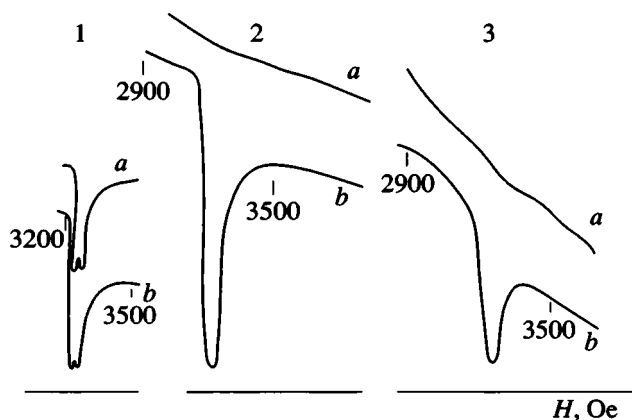


Fig. 2. EPR copper spectra in Co-bearing (1) acid, (2) intermediate, and (3) basic glasses under (a) initial and (b) heated conditions (at 500°C in the air).

lasted 6–12 h. At liquidus temperatures, glasses were synthesized, whereas at subliquidus temperatures, the partially crystallized glass-ceramics were derived. Part of the synthesized and natural sulfide-bearing dacites along with their sulfide constituents (grains of 150–500 μm across) were air-heated in alundum tubes at 500°C for 10 days. Then, the initial and heated solutions were treated with HCl solutions.

Table 1 lists the chemical and mineralogical compositions of studied systems. Table 2 lists weighted samples of glasses, glass-ceramics, natural rocks and extracted sulfides, amount of HCl solution and duration of its interaction with samples, and copper contents in phases.

Because Cu is a polyvalent element, oxygen potential is one of the major factors controlling the occurrence mode and behavior of this element in the processes considered. Therefore, all experiments were carried out at buffered f_{O_2} typical of natural conditions: Ni–NiO buffer for magmatic processes and atmospheric f_{O_2} for postmagmatic stage.

Based on thermodynamic calculations of the oxygen fugacity for metal–oxide and oxide (1)–oxide (2) systems as a function of temperature (Fig. 1), copper may occur in different oxidized states within indicated range of O_2 potentials (Durasova and Ryzhenko, 1992). If the Gibbs free energy difference between Cu^{2+} and Cu^+ in the aluminosilicate glass are similar to that of simple oxides, the same assumption may be made for volcanogenic rocks.

The experimental procedure was published in (Durasova *et al.*, 1987, 1994). To analyze the chilled phases, we used the following methods: X-ray microprobe analysis (analyst K.I. Ignatenko), electron paramagnetic resonance method (analyst V. K. Belyaeva), luminescence analysis (analyst E.N. Vasil'eva), atomic emission spectrometric spectroscopy with photoelectric device (analyst S.M. Chernogorova), atomic absorption spectroscopy (analyst T.V. Shumskaya), gas chromatography (analyst A.Kh. Galuzinskaya), electron spectroscopy for chemical analysis (analyst A.E. Shchukarev), and X-ray diffraction (analyst T.P. Kuznetsova).

EXPERIMENTAL RESULTS

Let us consider the results of investigations of copper state in glasses, which are compositionally similar to major rock types and were synthesized at liquidus temperatures under f_{O_2} of Ni–NiO buffer. In a series of runs, iron, which prevents the EPR determination of bivalent copper, was replaced by cobalt. The influence of Fe^{2+} replacement by Co^{2+} on the change of copper valency might be negligible because of their similar electron potentials. Fig. 2a demonstrates parts of the EPR Cu^{2+} spectra, recorded with SE/X-2544 spectrometer (*Radiopan*) at 300 and 77 K. In samples synthesized at the Ni–NiO buffer, signal of bivalent copper was discovered only in acid glasses. The copper state also was studied in Na–K–Si–Al–O glasses with luminescence spectra recorded at 300 K with an SDL-1 spectrometer and FEU-39 as a radiation detector. Luminescence was excited by ultraviolet light of a mercury–quartz lamp SVD-120A with URS-1 and Cl_2 (gas) light filters, which allowed us to distinguish the 254 nm mercury band more often used to excite the luminescence in glasses. Cu^+ luminescence intensity in samples synthesized at f_{O_2} of Ni–NiO buffer is nearly 13 times as high as that of a standard sample synthesized at air f_{O_2} (Fig. 3). This indicates that copper in the glass obtained at the Ni–NiO buffer is

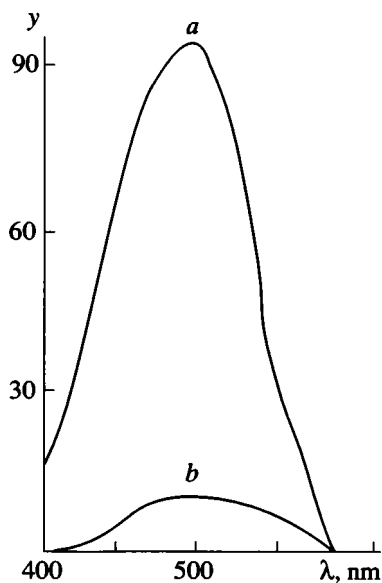


Fig. 3. Cu^+ luminescence spectra ($\lambda = 500$ nm) in acid glasses synthesized (a) at Ni–NiO buffer and (b) in atmosphere.

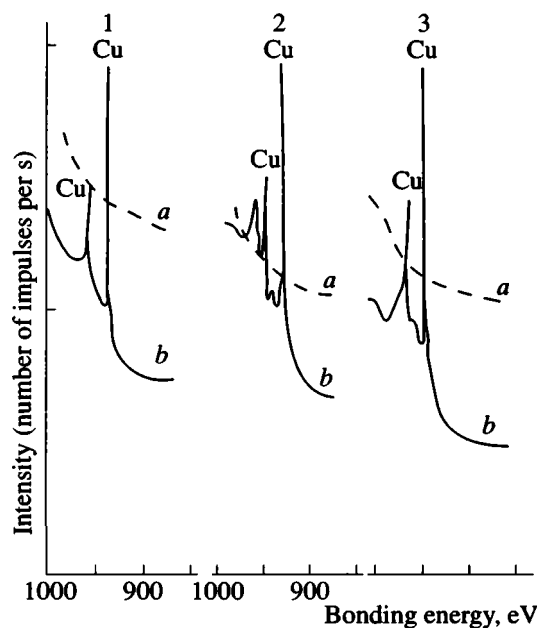


Fig. 4. ESCA spectra in (1) acid, (2) intermediate and (3) basic glasses under (a) initial and (b) heated conditions (at 500°C in the air).

predominantly represented by Cu^+ . The ESCA method indicates no copper enrichment of the surface of primary grains of synthesized glasses (Fig. 4a).

Data on solubility limits of Cu in acid (Ryabchikov *et al.*, 1984) and basic melts at Ni–NiO buffer show higher activity, particularly in the basic melts (Fig. 5). The solubility increases with increasing f_{O_2} . Obtained copper contents in melts are considerably higher than Clarke ones in the volcanogenic rocks (Vinogradov, 1961). Cu-rich layers were found in these samples with ESCA method (Fig. 4). Based upon ion microprobe analysis, Cu-rich layers are 110–210 nm thick.

We may estimate the modes of copper occurrence in studied natural samples, which were altered to pyrite-bearing sericite and quartz–sericite–quartzite metasomatites at 200°C (Karpukhina and Baranov, 1995), only with indirect data, such as thermodynamic estimates of f_{O_2} of the rock formation obtained from

determination of pyrite stability field. Based upon these data, we may suppose that in the initial samples copper occurs in Cu^+ form (Fig. 1).

Table 2 lists experimental data on the interaction between samples and HCl solutions; and Figs. 6a and 6b displays the amount of copper extracted from synthesized acid, intermediate, and basic glass and glass-ceramics; Fig. 6c and 6d shows the amount of copper extracted from metasomatic volcanogenic rocks and sulfides separated from them. A considerable mobilization of copper by HCl solutions from air-heated phases without any change in their petrochemical composition is observed. The highest copper loss from synthesized samples (both glasses and glass-ceramics) is typical of intermediate and basic varieties, and, to a lesser degree, acid rocks. High copper mobilization also was found in air-heated volcanogenic rocks. A considerable part of Cu was obtained from the sulfide component.

Table 3. Copper distribution in the pillow-lavas (Govett, 1983)

Sampling location	Number of samples	Cu in pillow (ppm)	
		in the core	near the surface
1	8	89	87
2	13	39	163
3	23	51	291

Note: (1) From background samples; (2) at 1 km from mineralization site; (3) at 10 km from the ore body.

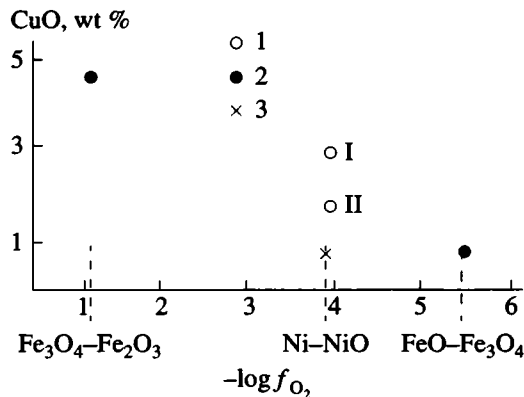


Fig. 5. Copper solubility at different f_{O_2} of the Ni-NiO buffer. (1) Boninite melt, $T = 1200^\circ\text{C}$; (I) ferruginous, (II) cobalt; (2) subalkaline melts, $T = 1200^\circ\text{C}$; (3) granite melt, $T = 750^\circ\text{C}$ (Ryabchikov *et al.*, 1984).

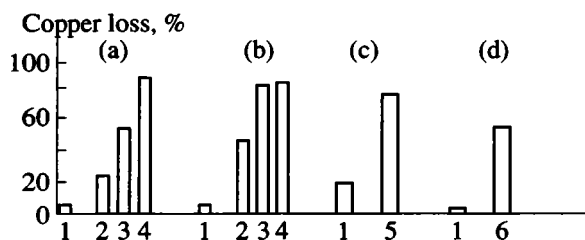
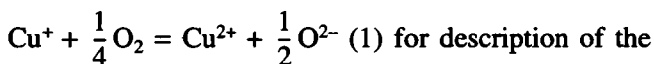


Fig. 6. Copper loss from (a) the initial and heated glasses, (b) ceramics, (c) volcanogenic rocks, and (d) their sulfide component. (1) Primary phases; heated (at 500°C in the air for 10 days) samples: (2) acid, (3) basic, (4) intermediate, (5) volcanogenic rocks, (6) sulfide component of the rocks.

THERMODYNAMIC ANALYSIS

Thermodynamic study of redox equilibrium for $\text{Cu}^+/\text{Cu}^{2+}$ in the aluminosilicate glasses at synthesis temperature indicates the applicability of equation

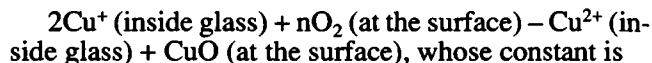


for description of the copper state in them—slight complex-formation tendency for both ions (Hirashima and Yoshida, 1961). Because Cu^+ has a spherical symmetry similarly to inert gas, it behaves in glass as a free ion. This might lead to high copper migration in glasses at change of thermodynamic parameters.

The physical mechanism of copper redistribution on heating at oxidized conditions is expressed in transportation of polyvalent element from the redox potential zone of the internal part to a different redox potential zone of the phase surface, which is in contact with gas atmosphere (in our case). The driving force of transportation is difference between chemical potentials (inside the phase and at its surface) of the polyvalent element form, in which it occurs in glass.

The amount of transferred atoms of such elements depends on a number of factors, including redox potential inside the phase and at its surface, oxidation degree, chemical composition and physical structure. The Cu^{2+} signal detected by EPR only in the heated acid glass, as well as lower copper mobilization by HCl solutions from heated varieties with respect to other glasses, are explained by specifics of the chemical composition and structure of glass. This is expressed in the relatively smaller amount of *non-bridge oxygen* and, respectively, NBO/T (non-bridge oxygen to tetrahedral cations) ratio (Barsukov *et al.*, 1983). According to reaction (1), the decreasing number of NBO shifts equilibrium into increasing Cu^{2+} content in the synthesized acid glasses. This presumably explains the specifics of copper behavior in the glasses, the occurrence of Cu^{2+} along with Cu^+ , as well as the weak migration ability of Cu on heating at oxidizing conditions, and respectively, lower extraction by HCl solutions.

Analysis of initial and air-heated samples allows us to express the proceeding transformations, oxidation, and redistribution of Cu as reaction:



$$K_1^0 = \frac{a\text{Cu}^{2+} (\text{inside glass}) \cdot 1}{a\text{Cu}^+ (\text{inside glass}) \cdot f_{O_2}^n} \quad (2)$$

From the equation, we obtain:

$$\frac{a\text{Cu}^{2+} (\text{inside glass})}{a\text{Cu}^+ (\text{inside glass})} = K_1^0 \cdot f_{O_2}^n$$

The most realistic, although ambiguous stoichiometric coefficient for this reaction seems to be 0.5. Because Cu^{2+} concentration (inside glass) is proportional to CuO (at the surface), oxygen fugacity near the aluminosilicate phase surface controls the proportions of polyvalent element forms in the aluminosilicate glass.

If the difference in Gibbs free energy between Cu^{2+} and Cu^+ in the aluminosilicate glass is similar to that of simple copper oxides and we follow the assumption that Cu^{2+} and Cu^+ do not form complexes in the glass (Hirashima, Yoshida, 1988), then oxygen fugacity in the $\text{Cu}_2\text{O}/\text{CuO}$ system represents an equimolar (in terms of activity) content of Cu^{2+} and Cu^+ in the aluminosilicate glass. Figure 1 shows the value above which the highvalent form becomes dominant. This estimate is approximate, because real energy of cations depends on anion framework and structure of the solid phase, as mentioned above. But it is useful to demonstrate the element capacity to be extracted from aluminosilicate rocks under influence of the redox potential in natural conditions. Similar copper behavior may occur on heating of sulfides in the volcanogenic rocks at oxidized conditions.

GEOLOGICAL IMPLICATIONS

Data on the geological study of Cyprus pyritic copper deposits and specifics of copper distribution in the volcanogenic rocks of the Troodos ophiolite complex is of great interest in the context of our experimental results. The lack of postvolcanic orogenesis and plutonic activity favor the revelation of distinct relations of these deposits with host ophiolite complex.

Most of these deposits are located either between upper and lower pillow-lavas or on the basal dike complex. In the latter case, orebodies are sharply depleted in Cu with respect to those located among pillow-lavas. The data reported on copper content in lava of the ophiolite complex indicate its clark values (Robinson *et al.*, 1987).

The study of copper distribution in separate metamorphosed pillows (Table 3) revealed that pillow cores near ore deposits are depleted in Cu relative to corresponding pillow (Govett, 1983). ^{18}O value of pillow margin are higher than that of pillow core (Fig. 6). Pillows, as a whole, are enriched in ^{18}O relative to fresh basalts ($^{18}\text{O} = +6$) (Spooner *et al.*, 1977). Thus, depleted specifics of copper distribution did not result from hydrothermal alteration degree and was presumably produced by another process.

We carried out experimental studies with aluminosilicate phases, which are compositionally similar to Cyprus pillow-lavas and were synthesized at $T = 1380^\circ\text{C}$ and f_{O_2} of Ni-NiO buffer, i.e., under conditions similar to those of formation of Troodos volcanogenic rocks (Durasova *et al.*, 1989; Sobolev *et al.*, 1986). We established that the heating of grains at high oxygen potential leads to increased element mobilization capacity. This results in depleted copper distribution, decreasing its content in pillow core, as well as the formation of highly soluble copper forms at the surface of some layers and cleavages. This mechanism is possible in the following natural conditions: (1) presence of primary volcanogenic rocks containing reduced Cu, (i.e. formed under lower f_{O_2} than that of Ni-NiO buffer); (2) minor jointings formed during both magma cooling and their following crushing and (3) heating under more oxidizing conditions (f_{O_2} higher than that of Ni-NiO buffer).

Experimentally revealed specifics of copper behavior allow us to evaluate the role of the volcanogenic rocks as copper sources in a new aspect, and to note the importance of heating stage in their geological evolution during redox potential change. The latter facilitates the copper transfer from disseminated form into concentrated one and lead to increasing ore-generating capacity of the rocks with respect to Cu (Durasova *et al.*, 1992; Durasova *et al.*, 1994).

We roughly evaluated the scales of copper transfer with gas-vapor phase and solid constituent during eruption of small Eldfell Volcano, Iceland.

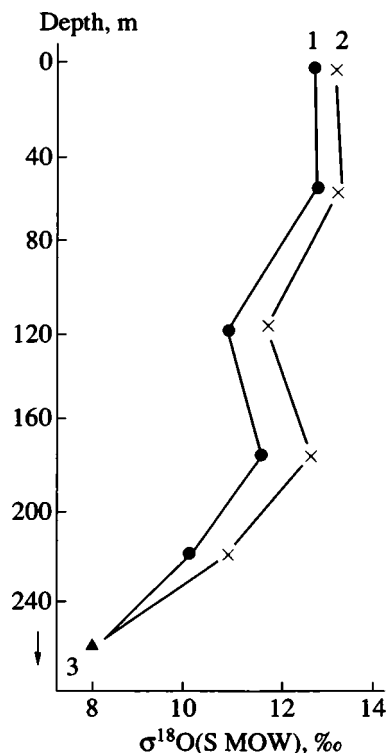


Fig. 7. $\delta^{18}\text{O}$ variation in the metamorphosed pillow-lava (Spooner *et al.*, 1977). (1) Core; (2) margin; (3) metadolerite dike.

Calculations of the oxygen potential during eruption (based upon gas equilibria and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in lavas) suggest buffer range of QFM-Ni-NiO (Barsukov *et al.*, 1990). According to the obtained data, copper should be in reduced species. At copper concentration of 0.05 ppm in fluid and 44 ppm in lavas and ashes (Durasova *et al.*, 1988), copper loss during eruption (volume of the erupted material is 0.25 km^3 or $750 \times 10^6 \text{ t}$, gas phase constitutes 5% or $37.5 \times 10^6 \text{ t}$) is 2 and 32000 t, respectively. But according to experimental data, copper amount, which may be extracted from the rocks during postmagmatic stage on heating under oxidizing conditions, is evaluated to be more than 15000 t. As experiments at 10 kb indicate (Durasova *et al.*, 1994), these values are comparable with that of magmatic fluids, which are released at upper mantle-lower crust depths, and are several orders greater than the amount of the gas component during eruption.

CONCLUSION

When an increase in temperature and change of redox potential occur during postmagmatic history of the magmatic rocks, ore-generating capacity with respect to Cu may increase by a factor of several times against the background of constant petrochemical composition. The inflow of acid solutions into these rocks

may result in a considerable copper enrichment and formation of metal-bearing thermes.

ACKNOWLEDGMENTS

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REFERENCES

- Barsukov, V.L., Durasova, N.A., Ryabchikov, I.D., Khramov, D.A., and Kravtsova, R.P., Specifics of Tin Behavior during Liquefaction of the Aluminosilicate Melt, *Geokhimiya*, 1983, no. 2, pp. 189–192.
- Barsukov, V.L., Durasova, N.A., and Dorofeeva, V.A., Evaluation of Oxidizing-Reducing Conditions of Present-Day Basalt Eruptions in Iceland, *Chem. Erde*, 1990, vol. 50, pp. 192–197.
- Durasova, N.A. and Ryzhenko, B.N., Thermodynamic Parameters of the Redistribution Processes of Some Ore Elements in the Aluminosilicate Systems, *Geokhimiya*, 1992, no. 12, pp. 1462–1467.
- Durasova, N.A., Belyaeva, V.K., Ignatenko, K.I., and Kravtsova, R.P., Solubility and Modes of Copper Occurrence in the Aluminosilicate Melts, *Geokhimiya*, 1987, no. 6, pp. 895–900.
- Durasova, N.A., Barsukov, V.L., Vakin, E.A., Kolesov, G.M., and Kravtsova, R.P., Metal Potential of the Products of the Eldfjall Volcano Eruption (Iceland), *Geokhimiya*, 1988, no. 2, pp. 192–197.
- Durasova, N.A., Belyaeva, V.K., and Ignatenko, K.I., Distribution and Modes of Copper Occurrence in the Boninite-like Melts, *Geokhimiya*, 1989, no. 7, pp. 1050–1055.
- Durasova, N.A., Belyaeva, V.K., Kochnova, L.N., Ignatenko, K.I., and Vasil'ev, E.N., Copper Migration in the Aluminosilicate Glasses on Heating as a Possible Source of the Copper Mineralization, *Dokl. Akad. Nauk SSSR*, 1989, vol. 308, no. 1, pp. 164–167.
- Durasova, N.A., Belyaeva, V.K., and Kochnova, L.N., Volcanogenic rocks—a Possible Source of Copper Mineralization at Thermometamorphism, *Geokhimiya*, 1992, no. 2, pp. 284–288.
- Durasova, N.A., Belyaeva, V.K., and Kochnova, L.N., RF Inventor's Certificate no. 2014639, 1994.
- Durasova, N.A., Ryabchikov, I.D., Kochnova, L.N., Belyaeva, V.K., and Ignatenko, K.I., Ore Potential of Fluids in the Deep-Seated Zones of the Earth, *Geol. Rudn. Mestorozhd.*, 1994, vol. 36, no. 6, pp. 565–569.
- Gandella, R.A. and Holland, H.D., The Partitioning of Copper and Molybdenum between Silicate Melts and Aqueous Fluids, *Geochim. Cosmochim. Acta*, 1984, vol. 48, no. 2, pp. 373–386.
- Govett, G.I., *Rock Geochemistry in Mineral Exploration. Hand Book of Exploration*, Amsterdam: Elsevier, 1983, vol. 3, pp. 305–313.
- Hirashima, H. and Yoshida, T., Redox Equilibria and Constitution of Polyvalent Ions in Oxide Melts and Glasses, *Glastechn. Ber.*, 1988, vol. 61, no. 10, pp. 283–292.
- Kamiya, K., Yoko, T., and Sakka, S., Migration of Cu^{2+} Ions in $\text{Cu}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ Glasses on Heating in Air, *J. Non. Crystal. Sol.*, 1986, no. 80, pp. 405–411.
- Karpukhina, V.S. and Baranov, E.N., Physicochemical Conditions of the Formation of the Pyritic Deposits of the Upper Uralian Ore District, Southern Ural, *Geokhimiya*, 1995, no. 1, pp. 48–63.
- Robinson, R.T., Gibson, Y.L., and Panayiotou, A., *Crystal Study Project: Initial Report Holes CY-2 and 2a Geological Survey of Canada*, 1987, Paper 85-29, pp. 155–235.
- Ryabchikov, I.D., Orlova, G.P., Mineeva, R.M., Bershov, L.V., and Korina, E.A., Copper and Silver in the Granitic Melt: Evidence from Experimental Data, *Geokhimiya*, 1984, no. 8, pp. 1181–1192.
- Sobolev, A.V., Tsameryan, O.P., Dmitriev, L.V., and Kononkova, N.N., Hydrated Komatiites as a New Type of the Komatiite Melts and Origin of the Ultramafic Lavas of the Troodos Massif, Cyprus, *Dokl. Akad. Nauk SSSR*, 1986, vol. 286, no. 2, pp. 422–425.
- Spooner, E.T., Beckinsale, R.D., England, P.C., and Senior, A., Hydration, ^{18}O Enrichment and Oxydation during Ocean Floor Hydrothermal Metamorphism of Ophiolitic Metasomatic Rocks from E. Liguria, Italy, *Geochim. Cosmochim. Acta*, 1977, vol. 41, no. 7, pp. 857–873.
- Vinogradov, A.P., Average Contents of Chemical Elements in the Major Igneous Rocks of the Earth's Crust, *Geokhimiya*, 1961, no. 7, pp. 556–565.

Rare Earth Elements and Scandium in Kuznetsk Basin Coals

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Abstract—This paper presents results of the study of concentration levels and distribution patterns of rare earth elements (REE) and scandium in coals of the Kuznetsk basin (Kuzbass). It is shown that these elements are unevenly distributed throughout the coaliferous sequence. This paper considers the relationship of REE and Sc with mineral and organic components, arriving at the conclusion that organic matter plays an important role in the accumulation of these elements. The share of REE and Sc concentrated in organic matter varies in different coal seams of Kuzbass from 20 to 60%, sometimes reaching 90%. It is suggested that the main accumulation mechanism for REE is integration into phosphate structure, and for Sc, chemisorption on organic matter and formation of metalloorganic complexes.

The Kuznetsk coal basin (Kuzbass) is one of the largest, best developed, and most promising basins in the world. Over 60 Mt of coal are extracted here annually (*Russian ...*, 1994), the processing of which produces enormous amounts of waste: clinker, ash, tailings, etc. Consequently, active environmental pollution takes place, which negatively affects the health of the populace. Only a small portion of waste products is economically utilized, mostly in construction engineering. At the same time, the problem of their complete utilization is highly pressing in some instances. One promising possibility is the comprehensive processing of clinker and ash refuse with concurrent extraction of useful components. For this purpose, it is preferable to use coal ashes enriched with economic metals, especially such valuable ones as Sc, REE, Ta, Ga, Zr, noble metals, and others. In view of the highly strained situation in Russia in respect to supplying our processing industries with Ti, Zr, high-grade aluminum raw materials, as well as Mn, Cr, and some REE ores (*Information ...*; 1993, *Strategic ...*, 1995; Trubetskoi, 1995), this approach may be considered highly auspicious.

The main reason restraining the extraction of these metals from the waste products of coal processing is their relatively low abundance. At the same time, it is known that even within one coal deposit, their concentrations in coal ashes from different seams may considerably vary, sometimes reaching considerable amounts (Yudovich *et al.*, 1985). The prediction and detection of such seams is a crucial task.

The Kuznetsk coal basin (Kuzbass), as one of the largest coal-mining regions of the country, has been attracting the attention of geologists for a long time as a potential source of rare and noble metals. As early as 1908, Kulibin (1908) suggested that ashes from a number of coal deposits of Kuzbass can be considered as a gold ore resource. In the 1940s, Shakhov and Effendi (1946) accomplished

specialized research which detected coal seams in Krapivino area, ashes which were enriched with valuable elements in commercially viable concentrations. At the same time, no investigations of Kuzbass coals providing reliable quantitative estimates of REE and Sc concentrations in them, much less revealing any regular patterns of their increased concentrations, have yet been accomplished.

The authors of this paper have been conducting comprehensive studies of the geochemical spectrum of various coal deposits in Kuzbass since 1989. This paper presents generalized data on the levels of concentrations and distribution patterns of REE and Sc in Kuzbass coals.

GEOLOGICAL CHARACTERISTICS

The Kuznetsk coal basin (Kuzbass) is located at the western margin of the Altai–Sayany folded zone. It is a depression surrounded by the mountain ranges of Salair, Gornaya Shoriya, and Kuznetsk Alatau, opening towards the West Siberia lowland. The basin is 26700 km² in area, 335 km long, and 110 km wide.

The geological setting of Kuzbass includes Paleozoic, Mesozoic, and Cenozoic sedimentary deposits. The main coal potential is associated with Upper Paleozoic (C₂–P) deposits of the Balakhna and Kol'chugino groups. They contain about 300 coal seams and interlayers with a maximum total thickness of 380–400 m. Of this number, 126 seams have commercial thickness. Both Balakhna and Kol'chugino groups comprise 6 formations each (Fig. 1). Outcrops of Permian–Carboniferous coal-bearing units are arranged almost concentrically (older units are located at the periphery of the basin, while younger ones are closer to the center) and form a vast synclinorium stretching from southeast to northwest.

Jurassic coal-bearing deposits (Tarbagan Group) at the present-day erosional surface remain only in separate troughs. Up to 56 coal seams have been discovered here, though only 5 to 14 of them are 0.8–9.0 m thick. Jurassic coals are not mined.

According to the degree of metamorphism, coals of both Balakhna and Kol'chugino groups are bituminous, with vitrinite content 30–60 and 60–90% respectively; the Tarbagan Group coals are brown, partially bituminous (the long-flame and gas ranks). The rank composition of bituminous coals varies over a wide range: from long-flame to anthracite. Their average ash content ranges from 7 to 20%. These coals are used both as technological raw material and high-grade steam fuel.

According to its mining, economic, and structural characteristics, the territory of Kuzbass is subdivided into 25 geoeconomic districts. Only 14 of them are engaged in active coal mining.

In the process of our investigations, we analyzed coals from different coal deposits in nine districts: Anzher, Kemerovo, Barzas, Uskat, Prokop'evsk–Kisilevsk, Aralichev, Osinniki, Mras, and Tom' Usa. The names of the sampled seams and their position within the coal-bearing sequence are shown in Fig. 1.

SAMPLING AND ANALYTICAL TECHNIQUES

Results of quantitative analysis of over 900 samples of coal and host rocks formed the basis of the research. Besides, most of the coal samples were incinerated, and their ashes were analyzed for a wide range of elements.

The investigation included sampling from 59 coal seams from different coal deposits of Kuzbass. Sampling of seams was carried out differentially; specific features of their structure were taken into account throughout the sequence, using the intermittent groove technique. Coals from the top, central and bottom part of a seam were analyzed separately, as well as the host rocks. Furthermore, individual coal units, various rock inclusions, interlayers, sulfide nodules, etc. were sampled separately. Lateral changes were studied on the basis of a network of cross sections.

In order to assess the geochemical nature of the accumulation of elements in coals, they were separated in a solution of tetrachloride of carbon into fractions by their specific gravity, spaced at 0.1 g/cm³, and then the fractions were incinerated at a temperature of 800–830°C in accordance with the standard GOST 1102275. The main technique used to detect concentrations of trace elements in coals and their ashes was neutron activation analysis carried out by the Nuclear Geochemical Laboratory of the Tomsk Polytechnical University (Laboratory Head E.G. Vertman, analysts A.F. Sudyko and others). The results of analysis of a standard sample ZUK-1 are given in Table 1. Moreover, all samples were analyzed by spectroscopic technique in the Central Laboratory of Berezovgeologiya (Novosibirsk), and control samples—by ICP method (St. Petersburg). The conver-

gence of the results of different analytical techniques is satisfactory. Conversion of the concentrations in ashes for coal and vice versa was used as an additional criterion of the quality of the data received.

The average concentrations of elements in coal seams were calculated as the weighted mean, with the sampling interval taken into account. The average estimates for separate formations and for the whole sequence were calculated as the arithmetic mean of the elements concentrations in coal seams and coaliferous formations respectively. The results thus obtained were checked against median and mode. In the case of a significant deviation, the mean values were checked against the median.

ANALYTICAL RESULTS

The investigation produced generalized geochemical characteristics of coals and host rocks for separate coal seams, deposits, coaliferous areas, and the whole Kuznetsk basin.

Levels of REE and Sc concentrations in the Kuzbass coals (Table 2) are, on the whole, comparable to the average data for coals world wide (Yudovich *et al.*, 1985).

Scandium is characterized by an average concentration of 4.1 ppm which is significantly higher than the value cited earlier of 1 ppm (*Metallogeniya* ..., 1988). It should be noted that the concentrations of this element in Kuzbass coals are higher than the average values for coals of the world (Yudovich *et al.*, 1985). Scandium abundances consistently increase from the bottom of the Balakhna Group upward, changing from 1.2 ppm in the Mazurovo Formation to 5.1 ppm in the Ustyat Formation. This phenomenon correlates well with the results of petrographic analysis of coal composition (Go Uin Lin, 1962). It was established that vitrinite content decreases with depth within the Balakhna Group sequence.

Furthermore, analysis of Table 2 reveals that the Balakhna Group is considerably enriched with HREE (Yb, Lu). It also contains an increased amount of LREE. It should be noted that the top part of the Balakhna Group contains twice as much La, Ce, Sm, and Eu than the bottom part of the Kol'chugino Group. It was also established that the Ustyat, Kemerovo, and Ishanovo formations of the Balakhna Group are more enriched with La, Ce, Sm, and Eu as compared to the Mazurovo, Uskat, and Kazankovo–Markino formations (Fig. 2). These data evidence that REE and Sc are distributed rather unevenly throughout the coaliferous sequence. This nonuniformity of distribution often becomes apparent within formations and sometimes even within individual seams. Levels of REE and Sc accumulation in coals and their ashes may differ by a factor of 2 to 5 (Table 3). The scatter of trace element concentrations within the individual seam is also significant.

Balakhna C _{2,3} -P ₁				Kol'chugino P ₂				Tarba-gan		Group					
C _{2,3} bl		P ₁ bl		Kuznetsk P _{1,2}	P ₂ it		P ₂ er		Subgroup						
Mazuro-vo	Alykai	Promezhu-tochnaya	Ishanovo		Kemerovo	Usyaty	Kazankovo-Markino	Uskat	Lenin	Gramotein	Tailugan	Formation	Thickness, m	Section	Number of dev-eloped seams
105-570	130-570	150-700	100-500	110-310	110-240	500-930	300-1150	300-510	500-650	380-600	700-800	500-800			
3-16			20-29				6-20		39-50						
Rumyantsev															
Koksovyi, Tonkii															
XX, XXI, XXVII, XXIX, XXX, XXXI, XXXII, XXXIIa, XXXIII, XXXIV, XXXV, Ishanovo															
VI, VIa, XI, XII, XIII, XIV, XVI, XVII, Volkov, Podvolkov I, II, Vladimir, Kemerovo, Lutugin, Bezymyanniy, Gorelyi, Prokop'evsk, Viktorov, Moshchnyi															
I, II, III, IV, V															
Polkoshtin—1, 4; Kandalep—1, 3, 4, 5; Elban—1, 2, 3, 4															
Elban—5; Elban—6; Elban—9a; Elban—10															
12															
19, 21, 26, 27															
Novyi															
Sampled seams															

Fig. 1. Stratigraphic scheme of coaliferous deposits of Kuznetsk basin (Kuzbass) and location of the sampled seams.

Detailed investigations reveal that maximum concentrations of Sc are associated as a rule with near-contact (i.e., top and bottom) zones of a sequence. REE distribution within a seam is generally different. Their maximum concentrations are usually confined to P-rich

sectors of the seam, though in some cases increased concentrations are also registered in near-contact zones (Fig. 3).

The importance of P in the accumulation of REE in coals is confirmed, for example, by the existence of a sig-

Table 1. Correlation of results of the neutron activation analysis of a standard sample of coal ash ZUK-1 and certificate data

Element	Mean values $\pm$ measurement error, %	
	certificate	INAA
Sc	0.0011 $\pm$ 0.0001	0.0013 $\pm$ 0.00002
La	0.0020 $\pm$ 0.0003	0.0019 $\pm$ 0.00001
Ce	0.0038 $\pm$ 0.0005	0.0032 $\pm$ 0.00002
Sm	0.00041 $\pm$ 0.00005	0.00037 $\pm$ 0.00001
Eu	0.00009 $\pm$ 0.00001	0.00013 $\pm$ 0.00001
Tb	0.000068 $\pm$ 0.000012	0.000090 $\pm$ 0.000008
Yb	0.00026 $\pm$ 0.00003	0.00025 $\pm$ 0.00001
Lu	0.000040 $\pm$ 0.000005	0.000044 $\pm$ 0.000001

Table 2. Average concentrations of REE and Sc in Kuzbass coals, ppm

Element	Coaliferous groups (Gr) and formations (Fm)								Average for the sequence
	Tarbagan Gr	Kol'chugino Gr			Balakhna Gr				
	Conglomerate Fm	Gramotein Fm	Uskat Fm	Kazankovo-Markino Fm	Usyaty Fm	Kemerovo Fm	Ishanovo Fm	Mazurovo Fm	
Sc	7.8	3.9	3.2	3.4	5.1	4.1	4	1.2	4.1
La	8.8	13.5	7.8	6.8	15.4	11.9	12.8	1.8	9.3
Ce	14.5	32.1	18.2	12.1	27.4	22.6	23.4	3.8	17.4
Sm	2.5	2.0	2.1	1.8	3.2	2.6	2.8	0.7	2.2
Eu	0.65	0.57	0.45	0.31	0.89	0.6	0.56	0.2	0.52
Tb	0.85	0.43	0.66	1.3	0.56	0.65	0.52	0.4	0.71
Yb	1.0	1.0	0.65	0.79	1.8	1.7	1.4	0.4	1.1
Lu	0.3	0.21	0.25	0.27	0.39	0.42	0.26	0.15	0.29
A ^d	17.3	15.6	15.6	12.3	13.5	12.3	11.9	7.6	12.2
n	2	16	72	32	87	60	34	2	305

Note: (A^d) ash content, %; (n) number of samples.

nificant positive correlation between these elements from seam II of the Usyaty Formation ($r = +0.45$), characterized by abnormally high concentrations of REE, Sc, and P. The sum of REE in some samples of coal ash here exceeds 0.1%; the contents of Sc and P are 0.01 and 8%, respectively.

Due to such vertical nonuniformity of elements distribution, examination of lateral variations in their concentrations throughout the basin is highly complicated. Table 4 demonstrates variations of REE and Sc concentrations in some geoeconomic districts of Kuzbass. These variations are quite significant. Average abundances in some cases differ by an order of magnitude. However, any conclusions on the lateral variations on the basis of these data would be incorrect, as in different districts productive seams often belong to different stratigraphic levels. Viable observations of such variations may be done only by tracing deposits belonging to the same formation or, actually, to one coal seam

across substantial distances. Table 5 shows variations in REE and Sc concentrations within the Usyaty Formation in the southern part of Kuzbass from west to east (Dmitrov mine–Shevyakov mine). Different ash content of coals hampers the analysis of the results obtained. Because of this, denominator shows conversions of concentrations for ashes. They evidence that REE and Sc concentrations in ashes gradually decrease eastward. It should be noted that these variations are meaningful only over considerable distances. Within one mine field or coal deposit lateral variations of elements concentrations are as a rule negligible (Fig. 4).

Investigation of REE and Sc concentrations in coals of different ranks (Table 6) revealed that the detection of any regular patterns while analyzing generalized results for the whole Kuzbass is highly problematic due to different environments of coal formation in different areas of the basin. Here, the leading role apparently belonged to the geochemical characteristics of pro-ve-

nances of ancient swamps. Such regularity can be reliably traced in a number of cases within a relatively small area.

For example, among those coals found in the Tom' Usa district there are coking, lean-baking, lean, and anthracite varieties. Composition of the host rocks differs insignificantly, and on the whole, the sedimentary sequence here can be characterized as uniform. Results of the analyses are given in Table 7. The numerator shows the initial data and the denominator—the results of calculations after elimination of the terrigenous component. The latter procedure was accomplished in order to display the role of the organic component in accumulation of elements and to highlight the significance of the metamorphic factor in their concentration. Evaluation of the terrigenous component share in an element accumulation in coal was accomplished with the help of a calculation technique based on the assumption that the composition of the terrigenous ash of the coal is close to that of the coal-hosting rocks and the heaviest coal fraction ($>1.8 \text{ g/cm}^3$), as well as on the supposition that the ash content of the lightest coal fraction is determined mainly by the presence of biogenic and sorption ashes. Knowing the total ash content, the share of biogenic and sorption component, as well as REE and Sc concentrations in the coal and host rocks, it is possible

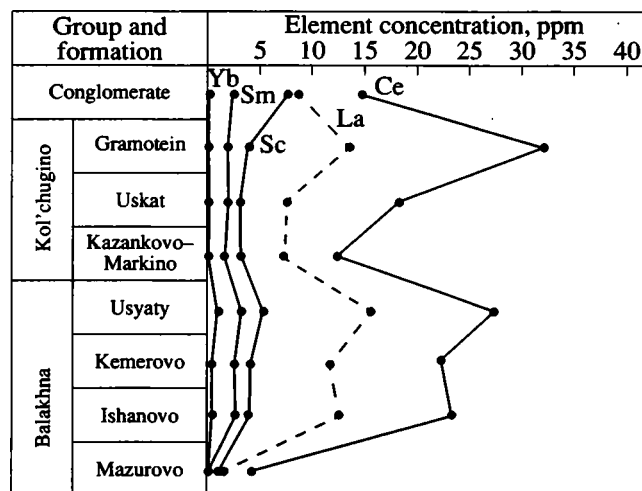


Fig. 2. Diagram showing changes in REE and Sc concentrations throughout the sequence of coaliferous deposits of Kuzbass.

to calculate the share of organic matter in the elements accumulation.

As it is clear from Table 7, the increase in the degree of coal metamorphism is characterized by a drop in REE and Sc concentrations. This tendency, with rare

Table 3. Concentrations of REE and scandium in coals and ashes from the Kemerovo Formation at the Ol'zhera deposit, ppm

Element	Coal seam						
	VI	VIa	XI	XII	XIII	XVI	XVII
Sc	$\frac{5.5}{17}$	$\frac{3.8}{21}$	$\frac{4.6}{22}$	$\frac{2.8}{23}$	$\frac{3.7}{26}$	$\frac{2.6}{39}$	$\frac{3.0}{30}$
La	$\frac{19}{80}$	$\frac{8.7}{63}$	$\frac{21}{80}$	$\frac{10}{75}$	$\frac{4.8}{44}$	$\frac{3.7}{65}$	$\frac{11}{157}$
Ce	$\frac{25}{134}$	$\frac{20}{76}$	$\frac{39}{102}$	$\frac{13}{83}$	$\frac{12}{63}$	$\frac{8.3}{66}$	$\frac{25}{242}$
Sm	$\frac{4}{15}$	$\frac{1.8}{14}$	$\frac{3.4}{15}$	$\frac{1.9}{13}$	$\frac{1.2}{11}$	$\frac{0.95}{13}$	$\frac{2.1}{20}$
Eu	$\frac{0.85}{3.1}$	$\frac{0.55}{2.6}$	$\frac{0.71}{2.9}$	$\frac{0.44}{2.8}$	$\frac{0.51}{2.7}$	$\frac{0.33}{3.7}$	$\frac{0.47}{4.3}$
Tb	$\frac{0.5}{2.1}$	$\frac{0.71}{1.4}$	$\frac{0.64}{1.8}$	$\frac{0.44}{1.9}$	$\frac{0.31}{0.95}$	$\frac{0.47}{1.5}$	$\frac{0.53}{5.6}$
Yb	$\frac{2.7}{7.3}$	$\frac{1.6}{9.3}$	$\frac{2.2}{9.2}$	$\frac{1.7}{9.1}$	$\frac{1.0}{8.0}$	$\frac{1.1}{13.0}$	$\frac{2.0}{10.0}$
Lu	$\frac{0.7}{1.4}$	$\frac{0.34}{2.2}$	$\frac{0.55}{2.0}$	$\frac{0.38}{2.0}$	$\frac{0.33}{1.7}$	$\frac{0.28}{3.3}$	$\frac{0.53}{1.6}$
A ^d	24.5	12.3	16.4	10.1	10	6	8.1
n	4	6	19	5	6	5	6

Note: (A^d) ash content, %; (n) number of samples. Numerator—concentrations in coal, ppm, denominator—concentration in ash, ppm.

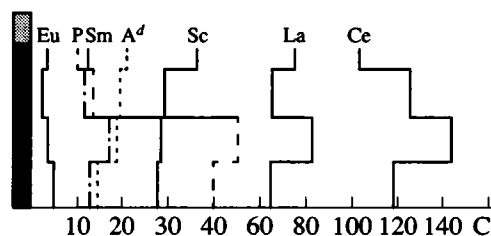


Fig. 3. Distribution of REE, Sc, P, and ash content (A^d) within the seam II section of the Usyaty Formation, Aralichev district. (C) Average concentrations: A^d in %, P in $n \times 10^{-10}\%$, other elements in ppm.

exceptions, is clearly manifested in the elements under investigation.

It was revealed that REE and Sc concentrations are also connected with the ash content of coals. It was noted that their concentrations rise with the increase of ash content. A positive, meaningful correlation between Sc concentrations in coals with their ash content was established. Research accomplished by Belyaev and Andrianova (1992) revealed the mathematical dependence of Sc concentrations of the ash content. For the Kemerovo Formation, it is described by the equation $Sc = 1.285 + 0.1235A^d$ with the correlation coefficient $r = +0.46$. According to our data on Kuzbass coals, on the whole, the equation has the following form: $Sc = 1.426 + 0.223A^d$ (Fig. 5).

At the same time, concentrations of these elements in ashes vary in inverse proportion to the ash content increase. Such relationships, according to Ryazanov and Yudovich (1974), indicate that terrigenous ash is the bearer, whereas sorptional and biogenic ash is the concentrator of elements.

For the purpose of assessing the role of organic matter in the accumulation of elements, coal was separated

into fractions by its specific gravity spaced at 0.1 g/cm^3 , which were then incinerated. Concentrations of the main trace elements were determined both in coal fractions and their ashes. The results are shown on Fig. 6. The figure demonstrates that maximum concentrations of REE and Sc are present in heavy high-ash coal fractions ($1.5\text{--}1.8 \text{ g/cm}^3$). There is a regular increase in the concentrations of elements with the increase of the specific gravity of fractions. At the same time, maximum concentrations in ashes are typical for low-ash light fractions. The coefficient for accumulation of light fractions in ashes in respect to the initial material varies from 1.5 to 3.0 for different elements. This indicates the important role of organic matter in REE and Sc concentration.

Chondrite-normalized standard REE spectra show the normal type of a distribution curve, practically indistinguishable in its form from calibrated curves for sedimentary deposits (Fig. 7). A slight tilt towards HREE can be noted in the normalized curves as compared to the normal distribution. The known geochemical coefficient La/Yb matches that of the sedimentary deposits of the Earth's crust, ranging from 7 to 14. This indicates the absence of any significant fractionation of the elements in the process of their accumulation. The Eu minimum is usually manifested only slightly or is not at all apparent.

DISCUSSION

Levels of the REE, Y, and Sc concentrations in Kuzbass coals are controlled by numerous factors, the leading of which are apparently the geological and geochemical environment of coal accumulation and the degree of transformation of the coal material.

The environmental factor is responsible for the formation of the initial geochemical background of a coal

Table 4. Concentrations of REE and scandium in coals from different geological and industrial districts of Kuzbass

Element	Geological-industrial district								
	I	II	III	IV	V	VI	VII	VIII	IX
Sc	1.2	4	3	7.3	3.8	6.5	3.5	4.3	4.6
La	1.8	10.2	10.1	12.1	11	17.3	7.1	14.3	16.3
Ce	3.8	23.9	20	35.8	30.7	28.9	13.9	25.9	33.8
Sm	0.7	2.2	3.1	5.5	4.5	2.9	1.9	3.5	2.9
Eu	0.2	0.6	0.7	0.9	0.6	1.2	0.35	0.6	0.7
Tb	0.4	0.4	0.3	n. f.	n. f.	0.5	1.1	0.6	0.7
Yb	0.4	1.2	0.95	0.83	0.97	1.9	0.8	1.5	2
Lu	0.15	0.25	0.37	0.01	0.02	0.38	0.25	0.31	0.5
A^d	7.6	8.2	n. f.	n. f.	n. f.	13.3	13.1	11.8	13.6
n	1	22	1	2	49	4	14	13	15

Note: (A^d) ash content, %; (N) number of sampled seams; (n. f.) not found. Geological-industrial districts: (I) Anzher, (II) Kemerovo, (III) Barzas, (IV) Uskat, (V) Prokop'evsk-Kisilevsk, (VI) Aralichev, (VII) Osinniki, (VIII) Mras-Su; (IX) Tom' Usa.

Table 5. Concentrations of REE and scandium in coals and ashes from the Usyaty Formation at various deposits of Kuznetsk basin, g/m

Element	Dmitrov mine	Mezhdurechensk open pit	Lenin mine	Shevyakov mine	Average for the south of Kuzbass
Sc	$\frac{6.5}{50}$	$\frac{4.4}{41}$	$\frac{3.6}{19}$	$\frac{6.2}{21}$	$\frac{5.2}{33}$
La	$\frac{17.6}{136}$	$\frac{12.5}{116}$	$\frac{17.5}{91}$	$\frac{21.1}{70}$	$\frac{17.2}{103}$
Ce	$\frac{28.9}{224}$	$\frac{23.5}{217}$	$\frac{32}{167}$	$\frac{48.7}{162}$	$\frac{33.3}{193}$
Sm	$\frac{2.9}{23}$	$\frac{3.6}{33}$	$\frac{2.9}{15}$	$\frac{3.7}{12}$	$\frac{3.3}{21}$
Eu	$\frac{1.3}{10.1}$	$\frac{0.7}{6.5}$	$\frac{0.7}{3.6}$	$\frac{0.6}{2.0}$	$\frac{0.8}{5.6}$
Tb	$\frac{0.48}{3.7}$	$\frac{0.67}{6.2}$	$\frac{0.52}{2.7}$	$\frac{0.9}{3.0}$	$\frac{0.64}{3.9}$
Yb	$\frac{1.9}{14.7}$	$\frac{1.6}{14.8}$	$\frac{2.1}{10.9}$	$\frac{2.1}{7.0}$	$\frac{1.9}{11.9}$
Lu	$\frac{0.39}{3.0}$	$\frac{0.37}{3.4}$	$\frac{0.44}{2.3}$	$\frac{0.6}{2.0}$	$\frac{0.45}{2.7}$
A ^d	12.9	10.8	19.2	29.5	18.1
n	41	12	34	11	98

Note: Numerator shows concentrations in coal, ppm; denominator shows concentration in ash, ppm; (A^d) ash content, %; (n) number of samples.

deposit, depending on the paleogeographic environment of coal accumulation, geochemical characteristics of rocks in the terrigenous provenance, and manifestations of magmatism, hydrothermal activity, etc. This explains, for example, the considerable variations in REE, Y, and Sc concentrations in the Anzher and Tom' Usa geosindustrial districts (Table 4).

The second factor determines the possibility of accumulation of metals by sorption on the coal matter. Numerous studies revealed that the sorption capacity of organic matter is directly proportional to the degree of its transformation or ordering (Yudovich, 1978). The results of these studies evidence that the increase of organic matter transformation in the process of diagenesis and coal metamorphism leads to the decrease of oxyc functional groups in the structure of carbonaceous matter and, consequently, to the decrease of its metal sorption capacity by more than one order of magnitude. This conclusion was experimentally substantiated for the platinum-group elements (Varshal *et al.*, 1995). Eskenazi (1993), who revealed the same tendency in respect to Mn, proved the possibility of its sorption on coal matter and noted that manganese concentrations decreased with the increase of coalification level. Similar results were received earlier for Ge (Issledovanie ..., 1972). In the process of studying the forms of the bond of Ge with coal, the investigators arrived at the conclusion that it is bound with coal organic matter by a stable

chemical bond through passive forms of oxygen of ether type. Vitrinitized coal components and low-metamorphosed coals were the richest in germanium, as well as in oxygen.

Analysis of the results obtained by us revealed that REE and Sc concentrations in coal ashes of Kuzbass are significantly higher than that in the host rocks. This points to the important role of the organic component in the general balance of elements and, consequently, to their typomorphism for coals (Yudovich *et al.*, 1985).

The share of biogenic and sorption components in the concentration of these elements was assessed through theoretic calculations, based on the data from the study of coal fractions. These calculations revealed that the role of

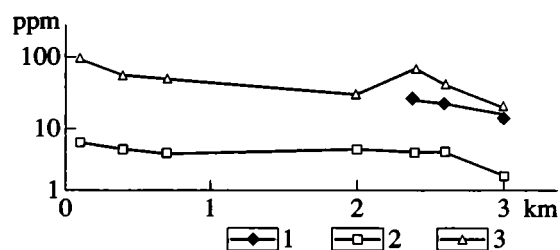


Fig. 4. Lateral changes in total REE and Sc concentrations in coal from seam XI (Tom' Usa district). (1) Ash content, %; (2) Sc concentration, ppm; (3) REE concentrations, ppm.

Table 6. Concentrations of REE and Sc in Kuzbass coals, ppm

Element	Rank of coal								
	LF	GF	F	C	SC	LB'	PB	L	A
Sc	7.8	5.3	3.7	4.6	3.1	4.6	3.8	4.6	2.7
La	8.8	11.9	7.8	11.7	7.7	16.1	10.3	13.9	7
Ce	14.5	30.2	16.2	29.8	22.6	29.6	26.2	26.9	45.6
Sm	2.5	3.6	2.3	3.6	2.7	3.5	2.8	4.5	1.3
Eu	0.65	0.74	0.39	0.6	0.38	0.75	0.63	0.7	0.55
Tb	0.85	0.65	1.2	0.6	n. d.	0.68	0.42	0.5	0.38
Yb	1	1.4	0.8	1.2	0.46	1.8	1.2	1.2	0.93
Lu	0.3	0.09	0.25	0.17	0.01	0.43	0.19	0.18	0.13
A ^d	17.3	n. d.	12.1	9.5	n. d.	15.8	8.2	12.8	7.8
n	2	43	44	107	5	76	26	74	3

Note: (A^d) ash content, %; (n) number of samples; (n.d.) not detected; (LF) Long-flame; (GF) Gas fat; (F) Fat; (C) Coking; (SC) Semicoking; (LB) Lean baking; (PB) Poorly baking; (L) Lean; (A) Anthracite.

sorption and biogenic accumulation of REE and Sc in coals is highly prominent and can reach 90% in Kuzbass coals, though usually it ranges from 20 to 60%.

The form of REE and Sc occurrence in coals is more complex. It is unlikely that there is only one form of

occurrence, and much more likely that there are several constituents here. While investigating the forms of element occurrence in coals, it is expedient to study their terrigenous and organic parts separately.

If accumulation of these elements in the terrigenous component is relatively well studied, the determination of the forms of their occurrence in organic matter is still a moot point. Some previous investigations have dealt with the forms of occurrence of Ge (*Issledovanie ...*, 1972), Au, PGE (Varshal *et al.*, 1995), and Mn (Eskenazi, 1993), and others. All these cases indicated the chemisorptional nature of the accumulation of these metals. It was noted that they are bound with organic matter by a stable chemical bond, evidently through passive forms of oxygen, consequently forming intricate metallorganic complexes. The number of such functional oxo groups decreases with the increase of the level of metamorphism and, as a result, the sorption capacity of coal in respect to metals also decreases.

The dependence between REE and Sc concentrations and coal ranks in the Tom' Usa district, shown in Table 7, apparently partially reflects this regularity. It is especially clearly seen after subtracting the share of the terrigenous component.

The facts cited above seeming to confirm the existence of a bond between REE and organic matter similar to that found in metallorganic complexes. At the same time, there are a number of cases in which a positive meaningful correlation between REE concentrations and phosphorus presence in the organic part of coal was registered. As previously noted by the authors (Arbuzov *et al.*, 1996), the highest REE concentrations were found in P-rich coals. This relationship can also be observed while studying coal fractions. Synchronism in changes of concentrations of REE and P is registered in coal fraction ashes.

Table 7. Concentrations of REE and Sc in coals from the Tom' Usa district of Kuzbass, ppm

Element	Rank of coal			
	C	LB	L	A
Sc	4.9	5.0	4.0	2.7
	3.7	3.1	2.5	1.8
La	16.0	17.1	15.1	7.0
	11.6	10.1	9.7	3.5
Ce	35.9	31.2	22.1	21.3
	29.7	21.3	14.1	16.3
Sm	2.8	4.0	3.3	1.3
	2.1	2.9	2.4	0.7
Eu	0.70	0.80	0.60	0.60
	0.54	0.54	0.39	0.47
Tb	0.80	0.68	0.55	0.38
	0.74	0.58	0.47	0.33
Yb	2.0	2.0	1.4	0.9
	1.6	1.4	1.0	0.6
Lu	0.49	0.47	0.26	0.13
	0.41	0.34	0.15	0.06

Note: (C) Coking; (LB) Lean baking; (L) Lean; (A) Anthracite. Numerator shows measured concentrations, denominator shows concentrations converted for organic matter.

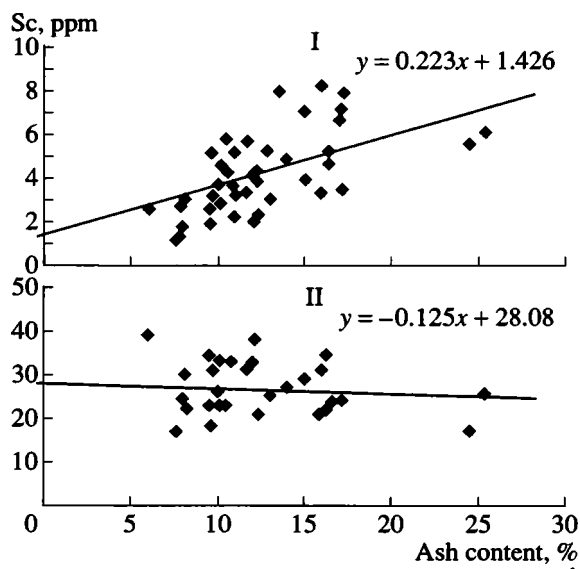


Fig. 5. Plots showing the dependence of Sc concentrations in (I) coal and (II) ash vs. ash content and regression equation.

It may be supposed that part of REE and Sc is isomorphically incorporated into phosphates formed in the course of coal formation. Sufficient quantities of P are present in the initial plant tissue, in which it amounts to 0.1–0.3% on the average, and in the plant ash its concentrations may reach 7% and even more (Voitkevich *et al.*, 1990). According to estimates by Alekseenko (1990), its concentrations in plant ash average 7%, and in some cases reach 12%. According to other investigators, dry plant matter contains 0.04 to 1% of phosphorus (Kist, 1987). In the process of coalification, most of it is lost. According to Kovalev and Zhukhovitskaya (1976), only about 4.5% of the phosphorus is actually buried. Furthermore, this element may be also brought from the outside together with the tuff material (Van, 1968).

Some free phosphate ions can interact with dissolved ions Ca^{2+} and Fe^{2+} , thus forming calcium and iron phosphates, capturing REE and Sc in the process. The mechanism of such precipitation of phosphate ions while interacting with ions of Ca and Fe was demonstrated on the example of peats from Volgograd region

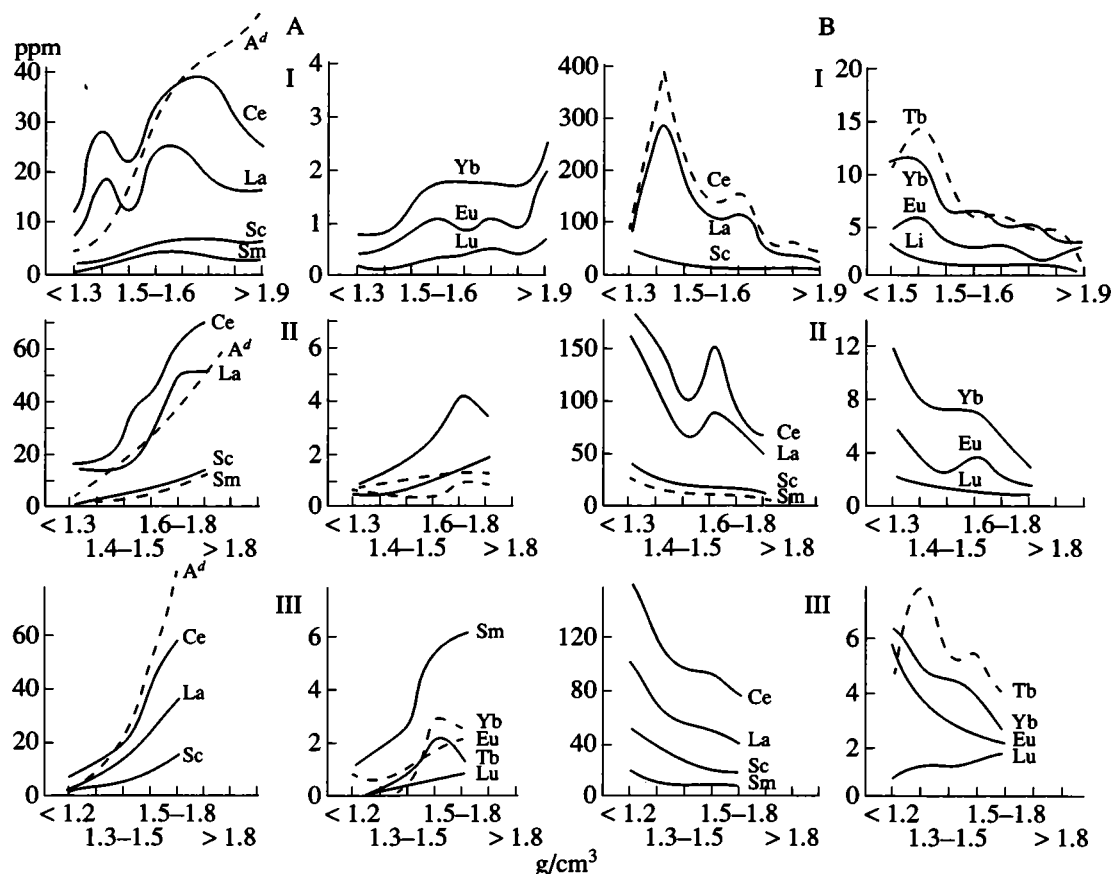


Fig. 6. Distribution of REE and Sc concentrations and ash content among (A) coal fractions and (B) ashes of fractions for coals of different ranks.

Coal ranks: (I) lean; (II) lean baking; (III) fat.

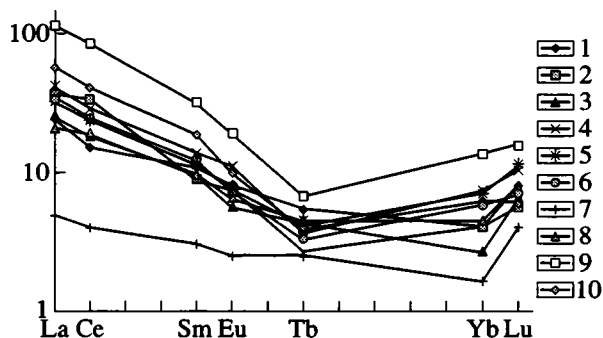


Fig. 7. Mean REE spectra of Kuzbass coals and European shales (Tailor and McLennan, 1988) and average sedimentary deposits (Balashov, 1976) (chondrite standard-normalized). Coaliferous formations: (1) Conglomerate, (2) Gramotein, (3) Uskat, (4) Usyaty, (5) Kemerovo, (6) Ishanovo, (7) Mazurovo; (8) average for the sequence; (9) shale from Europe; (10) average sedimentary deposit.

(Efimov *et al.*, 1993). Microinclusions of phosphates may impregnate coal matter, especially concentrating within plant parts initially enriched with phosphorus. This is attested by the discovery of fluorapatite microinclusions in gagate enriched with REE (Eskenazi, 1989).

Hence, it may be supposed that phosphates play a leading role in REE concentration in organic matter. Metallorganic compounds apparently also have a certain relevance.

Forms of Sc occurrence in organic matter are evidently somewhat different from those of REE. Here, the leading role apparently belongs to chemisorption following the pattern of the formation of complexes with a distinctly subordinate role of sorption accumulation on phosphates. Scandium, unlike REE, is an oxyphilic element, which is neutral towards phosphate ions, and in the case of precipitation, it is deposited in the form of hydroxides (Shmariovich *et al.*, 1989a) or as a part of organic complexes. This is corroborated by the results of chemical demineralization of coal carried out in the Moscow Mining Institute (Menkovskii *et al.*, 1968). According to these investigations, after treatment of low-ash coal fractions ($A^d = 6-8\%$) by hydrochloric and hydrofluoric acids, no more than 20% of Sc passes into the solution, which indicates a stable chemical bond of the bulk of the element with organic matter. Analysis of the group composition of coal revealed that the main mass of Sc is bound with humic acids.

Sources of REE and Sc may be either external, connected with solutions coming into a coal accumulation area, or internal. In the aggressive environment of peat bogs, part of the terrigenous material is dissolved, enriching the water of peat bogs with macro- and microelements. The possibility of the biogenic accumulation of elements should not be excluded either. The study of various plants revealed that in some cases, plants, and especially some of their parts, are much richer in REE than coals, and concentrations of elements in them can

reach 0.1–0.2% (Heskin *et al.*, 1968). It is known that moderate concentrations of REE affect plants favorably, and there is a number of plants able to accumulate these metals (Alekseev, 1987). In the process of coal formation, a considerable part of organic matter is removed. In an acid environment REE, Sc and other elements are easily leached out and become able to migrate (Shmariovich *et al.*, 1989b).

CONCLUSION

Our research showed that levels of REE and Sc concentrations in Kuzbass coals are comparable to the average data on the world coals. At the same time, a large group of seams here is characterized by abnormally high concentrations of these elements. In coal ashes from these seams, the REE concentrations can total 0.1% and even more, and Sc concentrations amount to 100 ppm.

Distribution of trace and rare earth elements within Kuznetsk coal basin is uneven both throughout the sequence and laterally, which is the result of geological and geochemical peculiarities of coal accumulation: rock composition at the provenances, distance from sources of terrigenous material, manifestations of magmatism, hydrothermal activity, etc. The largest REE and Sc concentrations are found in the coals from the top part of the sequence belonging to the Balakhna Group. The uneven distribution of elements throughout the sequence is typical not only for the Kuznetsk region on the whole, but also for separate formations and even individual seams. High REE concentrations are usually found in P-rich areas of seams, and Sc concentrations are higher at their contact zones. These facts should be taken into account when assessing the basin with respect to the content of trace and rare earth elements in it. It is necessary to study in detail the coal-bearing sequence of each mine field or deposit.

The REE and Sc, which are moderately typomorphic elements of coals, are often accumulated more in the organic, than in mineral part of coal. The share of REE and Sc concentrated in organic matter varies in different seams of Kuzbass from 20 to 90%.

The main mechanism of REE accumulation is supposed to be their incorporation into the structure of phosphates, and for Sc, it is mainly chemisorption on organic matter following the pattern of metallorganic complexes formation.

REFERENCES

- Alekseev, Yu.V., *Tyazhelye metally v pochvakh i rasteniyakh* (Heavy Metals in Soil and Plants), Leningrad: VO Agropromizdat, 1987.
- Alekseenko, V.A., *Geokhimiya landshafta i okruzhayushchaya sreda* (Landscape Geochemistry and Environment), Moscow: Nedra, 1990.

- Arbuzov, S.I., Potseluev, A.A., and Rikhvanov, L.P., Rare Earth Elements and Scandium in Coals of the Aralichev District in Kuzbass, *Geol. Geofiz.*, 1996, no. 3, pp. 68–73.
- Balashov, Yu.A., *Geokhimiya redkozemel'nykh elementov* (Geochemistry of Rare Earth Elements), Moscow: Nauka, 1976.
- Belyaev, V.K. and Andrianova, T.P., Regressive Analysis of Trace Elements with Quality Characteristics in Coal Seams of Kuzbass, *Razved. Okhr. Nedr.*, 1992, no. 3, pp. 11–12.
- Efimov, V.I., Kormilova, L.I., and Ibulayev, G.A., Role of the Main Components of Peat in the Sorption of Phosphate Ions, *Dokl. Ross. Akad. Nauk*, 1993, vol. 330, no. 4, pp. 502–503.
- Eskenazi, G., Phosphorus in Some Bulgarian Coals, *Spis. Bolg. Geol. Druzh.*, 1989, issue 50, no. 3, pp. 72–83.
- Eskenazi, G., Geochemistry of Manganese in Bulgarian Coals, *God. Sofiisk. Univ., Geol.-Geogr. Fak., Ser. Geol.*, 1993, no. 85, pp. 31–52.
- Go Uin Lin, Some Regularities in the Formation of Coal Seams in Coaliferous Strata of the Balakhna Group in Prokop'evsk District, Kuznetsk Basin, *PhD (Geol.-Miner.) Dissertation*, Moscow: Moscow Geological Prospecting Inst., 1962.
- Heskin, L.A., Frey, F.A., Shmitt, R.A., and Smith, R.Kh., *Distribution of Rare Earth Elements in the Lithosphere and Cosmos*. Translated under the title *Raspredelenie redkikh zemel' v litosfere i kosmose*, Moscow: Mir, 1968.
- Information on the State of Mineral Resources Basis and Geological Service of Russia, *Otech. Geol.*, 1993, no. 12, pp. 3–7.
- Issledovanie form svyazi germaniya s uglem i ego povedenie pri pirolize i szhiganiy* (Study of Various Forms of Bonds between Germanium and Coal, and the Germanium Behavior in Pyrolysis and Incineration), Novosibirsk: Nauka, 1972.
- Kist, A.A., *Fenomenologiya biogeokhimii i bioneorganicheskoi khimii* (Phenomenology of Biogeochemistry and Bioinorganic Chemistry), Tashkent: FAN, 1987.
- Kovalev, A. and Zhukhovitskaya, L., *Fosfor v bolotnoi srede (geokhimicheskie aspekty)* (Phosphorus in a Swamp Environment: Geochemical Aspects), Minsk: Nauka Tekh., 1976.
- Kulibin, K.A., Precious Metals in Bituminous Coal, *Zoloto Platina*, 1908, no. 24, pp. 510–511.
- Menkovskii, M.A., Komissarova, L.N., Guren, G.F., and Shatskii, V.M., Distribution of Scandium in the Products of Acid Demineralization of Bituminous Coal, in *Issledovaniya po khimii gornykh porod* (Studies in Chemistry of Rocks), Moscow: Nedra, 1968, pp. 38–42.
- Metallogeniya i geokhimiya ugleonosnykh i slantsenosnykh tolshch SSSR* (Metallogeny and Geochemistry of Coaliferous and Shaly Strata of the USSR), Moscow: Nauka, 1988.
- Russian Coal Overview, *Mining J.*, 1994, vol. 323, no. 8295, p. 130.
- Ryazanov, I.V. and Yudovich, Ya.E., Theory of Relationship between Admixture Elements Concentrations and Ash Content in Coals, *Litol. Polezn. Iskop.*, 1974, no. 6, pp. 53–67.
- Shakhov, F.N. and Effendi, M.E., Geochemistry of Coals of the Kuznetsk Basin, *Dokl. Akad. Nauk SSSR*, 1946, vol. 51, no. 2, pp. 135–136.
- Shmariovich, E.M., Polupanova, L.I., Natal'chenko, B.I., and Brovin, K.G., Behavior of Scandium in a Stratabound Infiltration Process of Mineralization, *Litol. Polezn. Iskop.*, 1989a, no. 1, pp. 83–92.
- Shmariovich, E.M., Maksimova, M.F., Brovin, K.G., and Polupanova, L.I., Behavior of Yttrium and Lanthanides in a Stratabound Infiltration Process of Mineralization, *Litol. Polezn. Iskop.*, 1989b, no. 6, pp. 39–57.
- Strategic Mineral Raw Materials of Russia, *Miner. Resursy Rossii*, 1995, no. 4, pp. 4–7.
- Taylor, S.R. and McLennan, S.M., *The Continental Crust: Its Evolution and Composition*, London: Blackwell, 1985. Translated under the title *Kontinental'naya kora: ee sostav i evolyutsiya*, Moscow: Mir, 1988.
- Trubetskoi, K.N., Current Status of the Raw Mineral Resources and Mining Industry of Russia, *Gorn. Zh.*, 1995, no. 1, pp. 3–7.
- Van, A.V., Role of Pyroclastic Material in Coaliferous Deposits of the Kuznetsk Basin, *Sov. Geol.*, 1968, no. 4, pp. 129–138.
- Varshal, G.M., Velyukhanova, T.K., Korochantsev, A.V., Tobelko, K.I., Galuzinskaya, A.Kh., and Akhmanova, M.V., Correlation between the Sorption Capacity of Carboniferous Material of Deposits in Respect to Precious Metals and Its Structure, *Geokhimiya*, 1995, no. 8, pp. 1191–1198.
- Voitkevich, G.V., Kokin, A.V., Miroshnikov, A.B., and Prokhorov, V.G., *Spravochnik po geokhimii* (Handbook of Geochemistry), Moscow: Nedra, 1990.
- Yudovich, Ya.E., *Geokhimiya iskopaemykh uglei: Neorganicheskie komponenty* (Geochemistry of Fossil Coals: Inorganic Components), Leningrad: Nauka, 1978.
- Yudovich, Ya.E., Ketris, M.P., and Merts, A.V., *Elementy-pri-mesi v iskopaemykh uglyakh* (Trace Elements in Fossil Coals), Leningrad: Nauka, 1985.

SHORT COMMUNICATIONS

The Basaltic Volcanic Ash in Paleocene Deposits of the Southern Volga Region

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Abstract—Upper Paleocene deposits of the Gromoslavka district in the Southern Volga region incorporate basaltic volcanic ash with black and brown glass. The thickness (10 cm) of the ash layer and the maximum size (0.2 mm) of ash particles suggest that the volcanic center was probably located at a distance of no more than several hundreds of kilometers in a cascade-type fracture zone that restricted the southeastern margin of the Voronezh Massif.

Ash units in the Cenozoic sedimentary cover of the East European Platform are described in several works (Akhlestina and Kuralev, 1988; Iosifova, 1992; Kalutskaya, 1980; Lodochnikov, 1935; etc.). Nevertheless, the problem of the ash source and possibility of the Cenozoic platform volcanism in this region is still controversial. The determination of the time of eruptions is also highly important, because such events can be related to strong tectonic rearrangements within both the platform and its periphery.

Volcanic ash units of basic composition encountered near the Gromoslavka and Verkhnyaya Buzinovka settlements (Fig. 1) in the Veshenka Formation, Volga region (Akhlestina and Kurlaev, 1988) have been poorly studied. The volcanic ash in Gromoslavka is of particular interest. Here, the 10-cm-thick ash layer is observed at outcrops of the Veshenka Formation over a distance of 325 m. These outcrops are located on the right bank cliffs 4.5 km downstream the Myshkova River.

The ash layer, along with diatomites at the top and sandstones at the bottom of the section are cemented by the sheaflike and spherulitic calcite. The aggressive calcite corrodes biogenic siliceous fragments, quartz and feldspar grains in host rocks, as well as volcanic glass in the ash layer. The calcite-cemented unit, which strongly differs from the host layer by its black color and high hardness, forms about 25-cm-thick erosional ledge.

The ash layer is represented by a group of small lenses composed of the silt- and fine sand-size glass particles. The moderate sorting of ash particles within each lens testifies to minimum rewashing of the ash layer, its separation by particle dimension, and transformation into a series of echelon-type sandy and silty lenses.

The ash material consists of fragments of transparent, brownish, spongy glass (refractive index 1.612 ± 0.003) and opaque, black-colored substance with a resinous luster (Fig. 2a). The brownish glass fragments contain spherical inclusions of black glass, crystals of pyroxene and olivine (Fig. 2b), and numerous gas

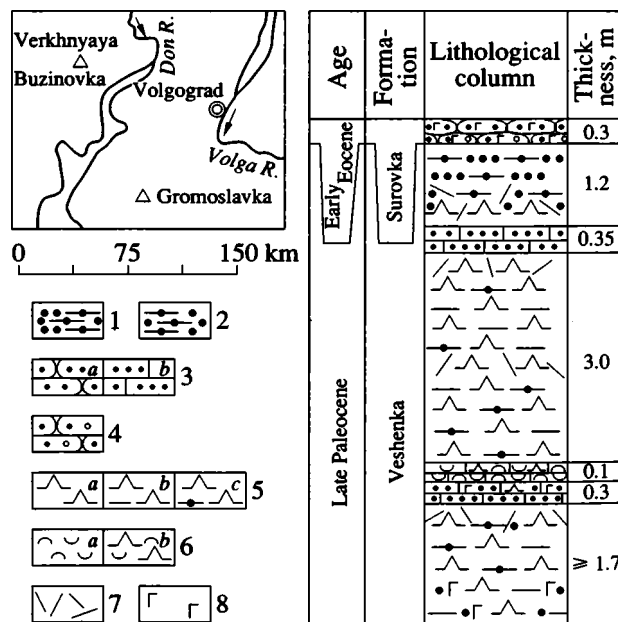


Fig. 1. Schematic location of Paleocene basic ash and the Veshenka Formation section near Gromoslavka. (1) Silty sand; (2) sandy silt; (3) sandstone with: (a) opal matrix, (b) calcareous matrix; (4) sandstone with opal matrix and inclusions of fine claystone pebble; (5) diatomite: (a) without admixture, (b) clayey, (c) silty; (6) basic ash with: (a) calcite matrix, (b) diatomite admixture; (7) acid ash admixture in rocks; (8) glauconite admixture in rocks.

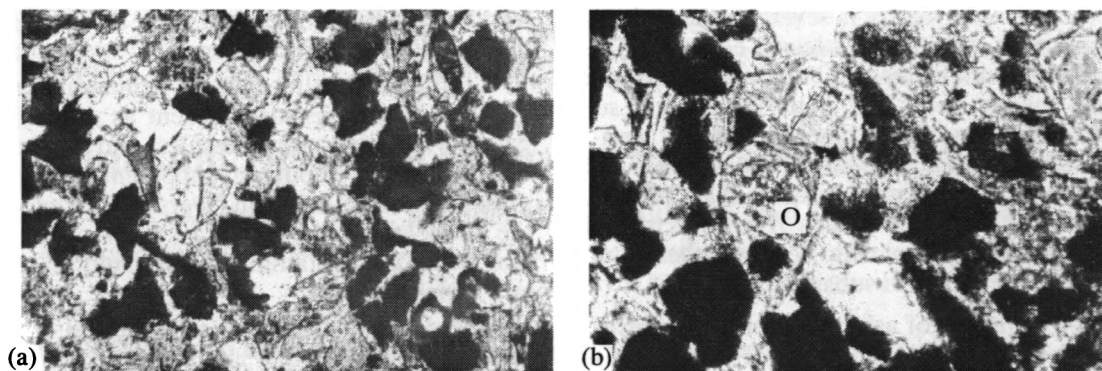


Fig. 2. Photomicrographs of the basic ash tuff. (a) Vitroclastic grains in carbonate matrix, magn. 100, transmitted light; (b) olivine (o) in glass fragment, magn. 300, transmitted light.

inclusions. The gravitational differentiation of brown and black glass masses at the preore stage was likely followed by their differentiation into less gas-saturated (black) and more gas-saturated (black) phases of glass at the eruption stage.

Microprobe analyses of the black and brown glass varieties are almost identical (see table). Even without taking into consideration the water, which is usually present in basalt glass, the total sum of oxides in black glass exceeds 100%. The inflated sum is probably induced by the absence of a glass-adequate standard in the microanalyzer or the presence of a free metal in the

glass. This assumption is indirectly corroborated by the presence of a magnetic property in black glass, promoting its refinement (up to 80%) with the application of a magnet. The color and opacity of black glass are most likely related to the dense dissemination of submicroscopic ore dust (magnetite, ilmenite, and metallic iron). In the brown glass segregations, the melt solidification was apparently rapid and older than the ore mineral crystallization.

In the case of platformal ash units, it is essential to locate the position of their parental volcanoes. Naturally, the area occupied by ash layers and, especially, an

Chemical composition of basic glass, %

Components	Microprobe data ¹				Bulk composition of glass ²
	black glass		brown glass		
	average of 5 analyses	range	average of 11 analyses	range	
SiO ₂	49.37	48.75–49.95	49.48	46.87–50.63	46.34
TiO ₂	3.93	3.72–4.25	3.91	3.65–4.60	4.26
Al ₂ O ₃	13.89	13.57–14.21	14.22	13.74–15.59	11.58
Fe ₂ O ₃	–	–	–	–	8.17
FeO	14.54	14.30–15.17	14.06	10.31–14.66	7.54
MnO	0.25	0.21–0.26	0.24	0.21–0.26	0.21
CaO	10.22	9.83–11.12	10.27	9.64–12.05	10.10
MgO	5.35	4.58–6.62	5.42	4.82–5.74	4.00
K ₂ O	0.73	0.53–0.93	0.77	0.30–1.01	0.86
Na ₂ O	2.25	1.70–2.94	1.98	0.92–2.90	2.28
P ₂ O ₅	0.64	0.53–0.99	0.62	0.50–1.08	1.14
H ₂ O ⁺	–	–	–	–	3.04
H ₂ O [–]	–	–	–	–	0.58
F	–	–	–	–	0.20
O = F	–	–	–	–	0.08
Total	–	100.12–102.81	–	98.11–102.58	100.22

Notes: ¹ Analyzed in IGEM by G.N. Muravitskaya. ² Analyzed in GIN by M.I. Stepanets. (–) not analyzed.

ash admixture in sand matrix is several orders of magnitude higher than the area of volcanic edifices. Moreover, volcanoes could be located both within intrabasin islands and ancient land. The study region was subjected to sea transgressions and regressions, as well as abrasional and erosional changes of the positive morphology; therefore, it is highly possible that the volcanoes could be destroyed during tens of millions of years after the termination of volcanic activity whereas ash layers could be preserved in subsidence areas.

The range estimates of ash migration from present-day volcanoes are given in (Fisher, 1964; Kalugin, 1967; Kir'yanov, 1983; Vlodavets, 1959; etc.). Based on these data and putting aside the attempt to locate the particular volcanic edifices, let us try to solve the equally important problem of the position of eruption centers *versus* the actually existing domains of ash layer distribution. These parameters are correlated with the intensity of eruption and the distance of observation point from the explosion center (Fisher, 1964; Gushchenko, 1986).

The diagram proposed by Gushchenko (1986) reflects the interrelation between various parameters, such as thickness of ash layer, maximum dimension of volcanic clasts, intensity of explosive ejection, and distance of the site from eruption center. Based on the available estimates, the maximum intensity of basaltic volcanic eruptions is not higher than the XII magnitude.

In our case, the basaltic particles with a maximum size of up to 0.2 mm compose a 10-cm-thick layer. Even if we assume that the eruption was of the maximum intensity (XII magnitude), which is possible for basaltic volcanoes, the ash material transport is only extrapolated up to a distance of several hundreds of kilometers. Therefore, it is unlikely that the ash material sources were located in the Caucasian, Crimean or Carpathian mountains. Hence, we assume that the basaltic volcanoes of the Volga region were located in other adjacent regions and probably associated with the intraplate deep faults that restrict the southeastern edge of the Voronezh antecline (*Karta* ..., 1978).

This assumption is corroborated by finds of lenses of volcanic basaltic ash near Verkhnyaya Buzinovka (Fig. 1) at a distance of 100 km to the north of Gromoslavka (Akhlestina and Kurlaev, 1988). The stratigraphic position of both ash units is identical; i.e., they are embedded in the Early Eocene (Akhlestina and Kurlaev, 1988) or Late Paleocene (Semenov, 1965) Veshenka Formation. Taking into consideration the late Thanetian age of diatoms from the ash unit and host diatomites in Gromoslavka, which were studied by I.E. Khokhlova, we accept the Late Paleocene age.

It should be noted that the acid glass (colorless, size up to 0.05 mm, $N = 1.50-1.51$) dissemination is ubiquitous in the Veshenka sequences of the Gromoslavka,

Verkhnyaya Buzinovka, and other districts in the Volga and middle Don river regions.

Clastic glass relics contain heulandite crystal overgrowths. Zeolite is also present as crystalline aggregates (within diatomite frustules) and admixture (in the clay matrix) without any apparent connection with glass fragments. Acid ash layers are not encountered in the study area, although all of the Veshenka sequence diatomites are contaminated with acid glass fragments to a variable extent.

The disseminated, acid ash material could be supplied by both proximal and distal provenances. However, the ubiquitous presence of ash particles in Upper Paleocene deposits of the study regions makes it possible to assume that the platform basaltic volcanism was a local episode against the background of a steady and intense volcanic activity in adjacent regions.

ACKNOWLEDGMENTS

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REFERENCES

- Akhlestina, E.F and Kurlaev, V.I., Eocene Ash Deposits in the Saratov and Volgograd Districts of the Volga Region, in *Voprosy geologii Yuzhnogo Urala i Povolzh'ya* (Problems of Geology of the Southern Urals and Volga Region), Saratov, 1988.
- Fisher, R.V., Maximum Size, Median Diameter and Sorting of Tefra, *J. Geophys. Res.*, 1964, vol. 69, no. 2, pp. 341-355.
- Gushchenko, I.I., Reconstruction of Pyroclastic Aerial Deposits, *Vulkanol. Seismol.*, 1986, no. 4, pp. 17-33.
- Iosifova, Yu. I., The Age of Ash-bearing Sequence near the Gorelka Settlement, Voronezh District, in *Stratigrafiya fanerozoia tsentra Vostochno-Evropetskoi platformy* (The Phanerozoic Stratigraphy on the Central East-European Platform), Moscow: Tsentrgeologiya, 1992, pp. 36-59.
- Kalugin, A.S., The Role of Volcanism and Reefs in the Bauxite Formation, *Litol. Polezn. Iskop.*, 1967, no. 1, pp. 3-22.
- Kalutskaya, S.A., The Cenozoic Bentonite Clays of the Voronezh Antecline, in *Bentonity* (Bentonites), Moscow: Nauka, 1980, pp. 64-73.
- Karta razlomov territorii SSSR i sopredel'nykh stran* (Map of Faults in the USSR and Adjacent Countries), Moscow: Mingeo SSSR, 1978, sheet 5.
- Kir'yanov, V.Yu., The Gravitational Eolian Differentiation of Ash from the Shevluch Volcano, Kamchatka, *Vulkanol. Seismol.*, 1983, no. 3, pp. 30-39.
- Lodochnikov, V.N., Semi-Loose Trachytic Ash Tuff from Duvanka, *Tr. TsNIGRI*, 1935, issue 39, pp. 19-34.
- Semenov, V.P., *Paleogen Voronezhskoi anteklizy* (Paleogene of the Voronezh Antecline), Voronezh: Voronezh. Univ., 1965.
- Vlodavets, V.I., Processes that Generate the Pyroclastic Material and Its Primary Dislocation, in *Problemy vulkanizma* (Problems of Volcanism), Yerevan: Akad. Nauk Arm. SSR, 1959, pp. 47-53.

SHORT COMMUNICATIONS

Unusual Uranium Concentrations in Paleovalleys

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Abstract—This work is devoted to the role of leucoxene and leucoxenized Ti-bearing minerals in the uranium accumulation during the infiltrational ore formation in paleovalleys.

The uranium sorption by titanium hydroxides may result in the origination of exotic uranium accumulations that are not directly related to the reducing geochemical barrier. These accumulations are characterized by the low solubility of U in acidic and alkaline solutions and, consequently, in their poor technological properties.

INTRODUCTION

One of the major commercial types of uranium deposits is represented by ore mineralization localized in buried, different-age paleovalleys. In Russia, deposits of this type are mainly confined to the Transbaikalian and Transural regions, where they have been explored by geological expeditions of the Geologorazvedka Concern for several years (Luchinin *et al.*, 1992). The formation of uranium ores in paleovalleys is related to the infiltration of underground flows of U-bearing oxic water along channel-facies sediments, consequent oxidation of primary gray-colored sediments, and formation of the ore-controlling geochemical zonality. Uranium and accompanying trace elements were accumulated on the reducing barrier as a result of the precipitation of low-soluble oxides and silicates of four-valent U.

BRIEF DESCRIPTION OF URANIUM DEPOSITS IN THE VITIM DISTRICT, TRANSBAIKAL REGION

On the Vitim Upland, Transbaikalian region, geologists of the GGP Sosnovgeologiya have discovered a large uranium ore district with deposits in Miocene paleovalleys (Luchinin *et al.*, 1992). Generally, uranium is present in deposits of the short-range (5–10 km) lateral tributaries of large paleorivers on the granite uplift slopes. The paleovalleys are filled with loose, poorly sorted, mainly arkosic clayey-sandy sediments accumulated as a result of the erosion of weathering products of granites.

The upper section of the sedimentary sequence consists of basic volcanics (tuffs, tuffites, and basalt lava interlayers). The total thickness of loose sediments attains several tens of meters. On a major part of the ore district, the loose, ore-bearing sediments are overlain by a basalt sheet up to 200 m thick. The plateau basalt succession can be divided into several flows separated by weathering crusts.

The ore mineralization, which is predominantly localized in basal layers of the gray-colored sediments

enriched in plant remains (C_{org} 0.8–1.5%), is governed by the stratal and ground oxidation zone including the subzone of yellow-colored and bleached rocks.

Genetically, the paleovalley-confined deposits are similar to well-known exogenous epigenetic deposits of Kazakhstan and Central Asia (Shchetochkin and Kislyakov, 1993).

The upper reaches of ore-bearing paleovalleys are located on slopes of the Baisykhan Uplift composed of Paleozoic granites, which most likely served as the source of U in ore-forming waters. Granites are characterized by a high uranium content (average 5.5–6.0 ppm) and high fraction of the mobile U. The uranium yield in the 5%-soda leachate from unaltered granites ranges from 30 to 50%.

In addition to the aforesaid commercial mineralization, some unique (unknown in other ore provinces) uranium ore occurrences are also encountered in the district studied.

ORE OCCURRENCES IN VOLCANIC EDIFICES

In the study district, prospecting works of the GGP Sosnovgeologiya have resulted in the discovery of 10 volcanic edifices governed by junctions of tectonic faults. The U-bearing paleovalleys were developed along some of these faults. Most of the volcanoes are not observed on the day surface, as they are buried under a sheet of plateau basalts.

The Vershinnyi Volcano located within the ore-bearing paleovalley is one of the largest and comprehensively studied edifices (Fig. 1). Originally, this volcano, whose upper section is eroded, represented a stratified tuffaceous cone that was later transformed into a collapse caldera due to subsidence onto the granite basement along steep faults. The caldera has a funnel-shaped morphology, and its diameter decreases from 450 to 100 m downward the cross section (Fig. 1).

The paleovolcano is composed of predominant basic tuffs and tuffites with an admixture of arkosic material. The caldera is crosscut by a series of diverse-

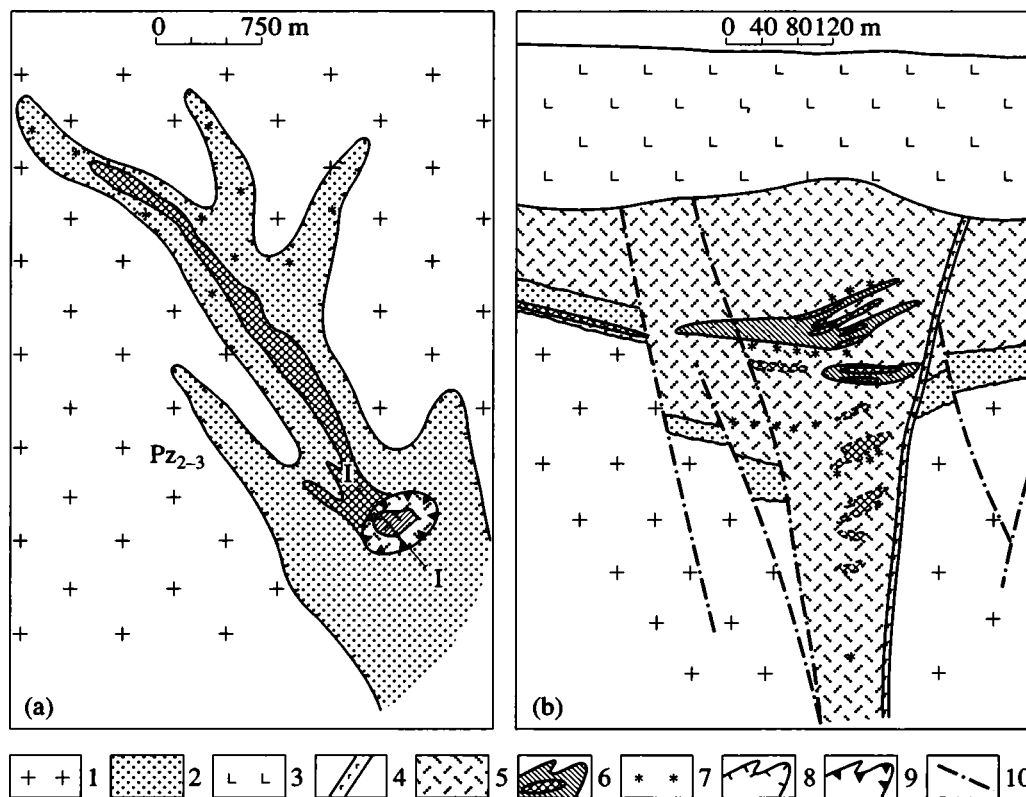


Fig. 1. Volcanic edifice in the ore-bearing paleovalley of the Vitim Plateau. (a) Plan view of paleovalley; (b) geological section across volcanic edifice. (1) Basement granites; (2) arkosic sediments of Miocene paleovalleys; (3) plateau basalts; (4) lamprophyre dike; (5) tuffs and tuffites; (6) ore bodies; (7) oxidation zone in paleovalley; (8) paleovalley boundary; (9) paleovolcano; (10) faults.

oriented faults and intruded by dike-shaped bodies of eruptive breccia, vitrophyric basalts, and dolerites.

The anomalous uranium concentrations in caldera can only arbitrarily be considered ores, because the uranium content (0.00n–0.0n%) does not attain commercial grade. As the uranium content of ore bodies is low, their boundaries are vague. The mineralization is mainly located at a depth of 110–210 m from the eroded volcano summit and is practically absent below this level.

A relatively increased uranium concentration is registered in flattened lenses and interlayers of tuffites enriched in coaliferous detritus and iron sulfides; therefore, one can infer that the mineralization is stratified to some extent. Ore-bearing layers are commonly more unconsolidated than barren ones and are characterized by increased water permeability. The mean contents of some components in tuffaceous sedimentary deposits of the paleovolcano are given in the table.

We paid special attention to the elucidation of the relationship between uranium concentration and superimposed diverse alterations that are widespread in the caldera. Clasts of tuffs and rock cement incorporate a wide range of neomorphous minerals, such as kaolinite, montmorillonite, hydromica, chlorite, siderite, zeolites, pyrite, leucoxene, etc. One can separate sectors with

different grades of mineralization; however, the intensity of metasomatic alterations is very weak and cannot be compared with the near-ore alterations at hydrothermal sites. We did not observe any relationship between neomorphous minerals and ore mineralization; sectors with the maximum hydrothermal alterations do not contain any appreciable uranium.

The uranium mineralization is characterized by a very fine-dispersed structure; therefore, it is not detected by ordinary optical methods. The fission radiography images demonstrate that track clusters are observed over the leucoxenized titanium minerals (ilmenite and sphene) along with oxidized siderite and iron hydroxides, which infill cracks, as well as coaliferous detritus and pyrite. The stringer uranium mineralization was not detected in any ore interval.

Trace elements are rare. Out of 85 ore samples, only 15 samples contain Mo (up to $1-2 \times 10^{-3}\%$), as well as Zn, Co, Zr, and Y (2–3 times more than the background values); i.e., the trace element spectrum is the same as in the ore-bearing deposits of paleovalleys.

Hence, the general pattern of uranium distribution in the volcanic edifice studied is distinct from the counterpart in hydrothermal ores in analogous structures; it is closer to the infiltrational model of ore formation.

Average content (in %) of some chemical components in tuffaceous sedimentary deposits of paleovolcano (80 samples)

Components	Na ₂ O	K ₂ O	MgO	CaO	TiO ₂	F	S _{total}	Fe	CO ₂	C _{org}	P ₂ O ₅
Content	2.0	1.7	4.6	4.7	2.4	0.1	0.1	6.6	4.7	0.4	0.5
Standard deviation	1.0	0.8	0.2	2.3	0.8	0.0	0.1	2.9	3.1	0.4	0.2

Presumably, uranium was supplied into the volcanic neck by ground waters that percolate along paleovalleys. The volcanic structure drained the flow of rather considerably reworked halo zone waters, from which most of the available uranium precipitated on the upper reaches of paleovalleys. However, even at such low uranium concentrations of distal ground waters, a subordinate amount of uranium was accumulated in the tuffaceous material. Since these waters contained minor amount of dissolved oxygen, their infiltration into volcanic neck was not accompanied by the formation of a well-developed, ore-controlling oxidation zone. This circumstance along with the absence of a contrast reducing barrier resulted in the vague boundary of mineralized zone. Obviously, uranium is mostly precipitated due to its sorption on high-absorption capacity components, such as clay minerals, hydroxides of Fe and Ti, and coaliferous detritus. We also cannot rule out the influence of reducing conditions (related to the presence of coaliferous detritus and iron sulfides) upon the degree of uranium yield from diluted solutions.

URANIUM CONCENTRATIONS IN BLEACHED BASALTS

Another, rather rare case of uranium concentration in the Transbaikalian region is observed at one of the ore occurrences near the eastern boundary of the plateau basalt domain. The ore-bearing arkosic sediments, which infill the erosional paleovalley, are overlain by a 15–20-m-thick basalt sheet consisting of two flows (Fig. 2). The lower basalt flow is strongly disintegrated by weathering processes and crosscut by a network of fissures into different-size blocks up to 0.5 m across. Each block is surrounded by a bleached rim a few centimeters in thickness. The bleaching intensity and rim width increase upward the lower basalt section; consequently, basalts are gradually transformed into clayey eluvium, whose relics are preserved in certain pockets (Fig. 2). The upper basalt flow is virtually unaltered by supergene processes.

Based on the mineralogical study, the bleached rim of lower basalts is composed of predominant clay minerals (montmorillonite, halloysite, and kaolinite) with an admixture of iron hydroxides and leucoxene. The rim is characterized by a high effective porosity (up to 40–50%).

The chemical analysis indicates an appreciable deficiency of certain petrogenic elements in the basalt rim: in the most altered samples, the amount of element export (calculated with the consideration of effective

porosity) is as follows (in %): FeO—96; MgO—90; CaO—70; Fe₂O₃—65; Na₂O—40; SiO₂—40. On account of the removal of these components, bleached basalts are relatively enriched in Ti (from 3.0–3.5% in unaltered basalts to 4.5–6.0% in bleached species). The aluminum content rises a few percents.

The data mentioned above suggest the supergene nature of the bleaching process. The hydrothermal or fumarole-solfatar argillization was not involved in the bleaching of basalts.

As in other ore-bearing paleovalleys, the major part of uranium mineralization in the study district is concentrated in arkosic, gray-colored sediments that infill the erosional valley. At the initial stage of study, the development of uranium mineralization in the overlying basalt sheet was a somewhat unexpected and inexplicable fact. The mineralized zone, which penetrates the lower section of basalt flow at a depth of 0.5–1.5 m from the top of the underlying bed of ore-bearing arkosic sediments, has a rather contrast upper boundary. As is evident from the macroradiographs, the uranium concentration, which is exclusively confined to bleached rims, varies within the same range, as in the case of sedimentary deposits of paleovalleys, i.e., within 0.0n–0.n% (Fig. 3).

Microradiographs of polished sections expose active centers (related mainly to leucoxenized ilmenite grains) and scattered tracks of U in clay material (Fig. 4).

The electron microscopy revealed a very high dispersion of uranium mineralization; therefore, the proper uranium mineral phase is difficult to recognize even at a magnification of 40000–60000. Bleached basalts, which overlie gray-colored sediments, contain minute (0.0n–0.n μm) segregations of the four-valent U. In general, uranium is present in an absorbed or other X-ray amorphous compound form, which is hard to identify, rather than an independent mineral phase.

The phase analysis demonstrated that uranium is strongly connected with substrate. Only 15–20% of total U in the sample studied is transferred into the 5%-solution of sulfuric acid. For comparison, we should mention that the uranium yield from commercial ores in paleovalleys in the aforesaid chemical condition is as much as 90–95%.

The U-rich ore samples from bleached basalts are characterized by high concentrations of trace elements that are typical of arkosic sediments in paleovalleys (in %): Mo up to 0.01; Zn up to 0.05; Zr 0.09; Co 0.1; and Th 0.005. Their content is one order of magnitude lesser in the barren, bleached basalts.

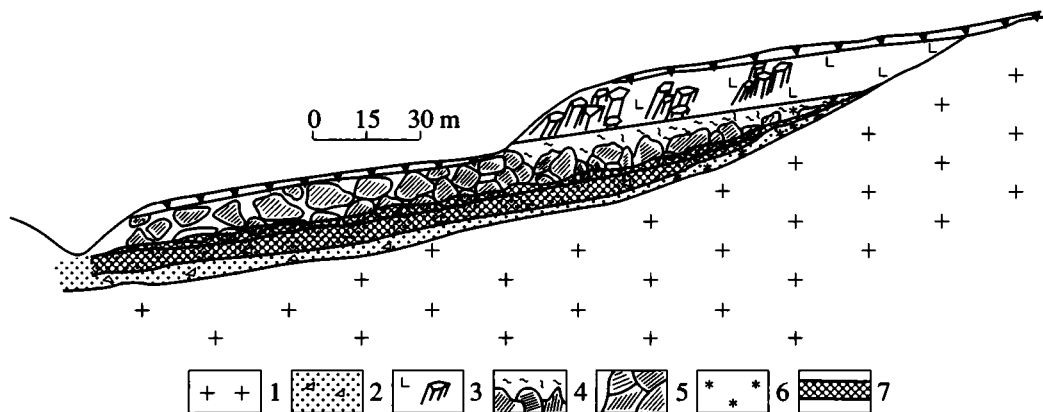


Fig. 2. Section across paleovalley with ore-bearing basalts. (1) Basement granites; (2) arkosic sediments of paleovalley; (3) plateau basalts; (4) weathering crust formed after the lower basalt flow; (5) weathered, disintegrated basalts of the lower flow; (6) oxidation zone at the upper reaches of paleovalley; (7) uranium mineralization in arkosic sediments and bleached basalts.

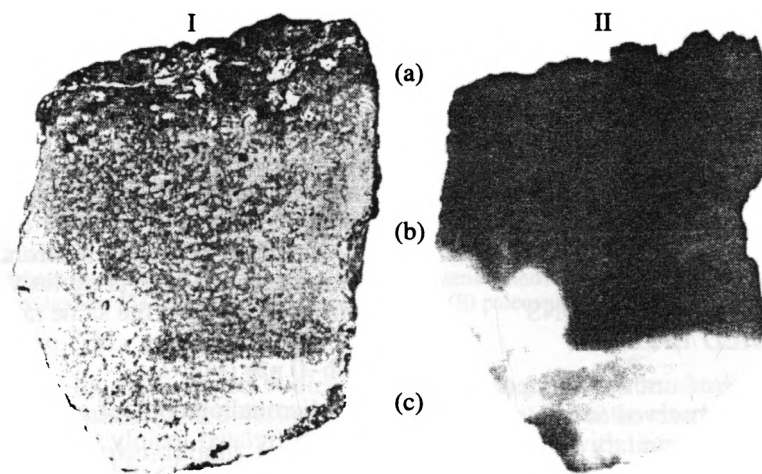


Fig. 3. Bleached U-bearing basalt. (I) Polished specimen (natural size): (a) unaltered basalt, (b) weakly altered basalt, (c) bleached shaly basalt; (II) macroradiograph, exposition 5 days.

Obviously, the uranium accumulation at the bottom of basalts was a consequence of the same infiltrational process that generated mineralization in the underlying arkosic sediments, and uranium was supplied by the same ground water flow that percolated along the erosional valley from the granite massif. Disintegrated basalts did not serve as aquiclude rocks. The ground water level within the basalt sequence governed the upper boundary of mineralization.

Prerequisites for the uranium accumulation in basalts were provided by their chemical weathering and disintegration that promoted the increase of their effective porosity and water permeability. The decomposition of ilmenite and other primary titanium minerals into amorphous oxides and hydroxides of Ti, which are the main concentrators of U, was also favorable for the uranium precipitation. This factor and the high content of U in ground waters were responsible for the appre-

ciably higher concentrations of U in bleached basalts than in volcanic neck tuffs. As may be judged from the mineral composition of weathered basalts including considerable iron hydroxides, uranium was accumulated in basalts in oxidizing conditions; therefore, ore occurrences in basalts are distinguished from the paleovalley counterparts and can be considered exotic formations.

The uranium accumulation in an oxidizing environment was described in only one work (Gavshin and Lavrent'ev, 1974). Based on electron microprobe data, obtained by these researchers, brown pelite samples from the red-colored Devonian sandstones contain 2.7–5.6% U and 1.5–1.9% TiO_2 ; U and Ti are directly correlated. Moreover, they noted a strange phenomenon: the U/Ti ratio in samples studied is higher than in the well-known uranium and titanium minerals.

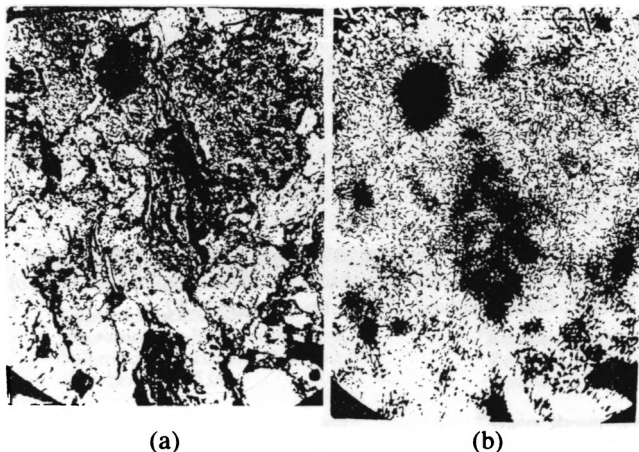


Fig. 4. Low-grade ore from the Dolmatov deposit. (a) Thin section, magn. 65, transmitted light. Dark spots are leucoxene inclusions in the kaolin cement of sandstone; (b) radio-graph in the Dacron detector showing track clusters over leucoxene.

As for the main commercial uranium ores in the Transbaikalian region paleovalleys, leucoxene, which is rare in the ore-bearing arkosic sediments, can hardly serve as a uranium concentrator. However, in other ore districts with specific geological conditions, this mineral is rather prominent as one of the chief concentrators of U in the ore-bearing paleovalleys.

LEUCOXENE-RELATED URANIUM CONCENTRATIONS IN THE TRANSURAL REGION DEPOSITS

The Dolmatov deposit thoroughly described in (Luchinin *et al.*, 1992) belongs to this group. The low-grade ore subzone (front part of ore lode) at this deposit contains leucoxene and leucoxenized ilmenite that play the role of chief uranium concentrators and incorporate 30 to 45% of total U in samples studied (Fig. 4). Even within a single sample, the concentration of U in leucoxenized ilmenites and leucoxene is highly variable and reaches up to 1.2–1.5% (based on the neutron activation analysis data). The low-grade ore subzone is noted by a direct correlation between U and Ti ($K = 0.75$, number of samples = 31). A similar correlation is observed in the oxidation zone, where the uranium content is generally low (0.00011–0.0011%) and the major part of U is concentrated in leucoxene grains. In high-grade ores, uranium is mostly encountered as independent mineral phases of uranium oxides and coffinite, whereas the contribution of leucoxene-related U is decreased and its correlation with Ti is lacking. It is noteworthy that an increased content of U (0.0n%) in leucoxene is also registered in the oxidation zone.

The electron microscopy revealed the heterogeneity of the internal structure and composition of leucoxenized ilmenite grains composed of prismatic and acicular crystals (0.0 μm) of ilmenite, rutile, anatase, and

goethite. Locally, they contain clots of X-ray amorphous, vitreous substance with considerable Ti and U. Cracks in leucoxene grains enclose fine-dispersed uranium oxides and coffinite.

The leucoxene-related uranium is difficult to extract into the alkaline or acidic leachates, i.e., it has a poor geotechnological property; in laboratory conditions, the uranium extraction from low-grade ores into the sulfuric acid solution is 40–60%, which is 1.5–2 times less than the respective value for high-grade ores.

CONCLUSION

Despite several differences in the geological setting, the above-described forms of uranium accumulation have a common feature related to the participation of leucoxene that represents a product of the destruction of primary titanium and Ti-bearing minerals, including ilmenite. During supergene alterations and chemical weathering, in particular, the Ti-bearing minerals are replaced by amorphous oxides of Ti and Fe with a high absorptivity.

Based on experimental data, the amorphous, fresh precipitate of titanium hydroxide can extract up to 70% of total U in sea water; the maximum capacity of the sorbent was 7.3% U (Kas'yanov *et al.*, 1975). Obviously, such a process is also possible in the natural state in a wide range of both reducing and oxidizing physicochemical environments.

After the termination of supergene processes and burial of leucoxene-bearing sediments, amorphous compounds can be subjected to a partial or complete recrystallization and formation of secondary oxides, such as sphene, rutile, and anatase (Sochneva, 1970). Therefore, mineralogical guidebooks define leucoxene as a blend of the aforesaid minerals and amorphous substance.

The composition of leucoxenes studied also varies in different regions. Leucoxenes are composed of only an amorphous substance in bleached basalts from the Transbaikalian region, while they consist of predominant secondary titanium oxides at the older Dolmatov deposit.

As a result of recrystallization of titanium hydroxide, uranium is precipitated as an independent mineral phase, but a significant part of U is combined with Ti to form low-soluble, amorphous compounds.

The very strong capacity of titanium hydroxide to accumulate and retain U in a wide range of geochemical conditions may result in unusual uranium concentrations that are not directly related to the reducing barrier. This property of titanium hydroxide is unique, inasmuch as high concentrations of U (except for secondary halos at uranium deposits), similar to those in leucoxenes, are not formed in oxidizing conditions in all other well-known natural sorbents, such as brown coal, hydroxides of Fe and Al, calcium phosphate, clay minerals, etc. Unfortunately, the strong bond of U with

leucoxene hampers the technological treatment of titanium hydroxides.

REFERENCES

- Gavshin, V.M. and Lavrent'ev, Yu.G., Uranium-Titanium Correlation in Cryptocrystalline Pelite, *Geokhimiya*, 1974, no. 2, pp. 243-247.
- Kas'yanov, A.V., Bezborodov, A.A., and Zhorov, V.A., Coprecipitation of Uranium with Titanium Hydroxide from Sea Water, *Radiokhimiya*, 1975, vol. 17, issue 4, pp. 477-481.
- Luchinin, I.I., Peshkov, P.A., Dement'ev, P.K., Kochenov, A.V., Khaldei, A.E., and Khalezov, A.B., Uranium Deposits in Paleovalleys of the Transural and Transbaikal Regions, *Razved. Okhr. Nedr*, 1992, no. 5, pp. 12-15.
- Shchetochkin, V.N. and Kislyakov, Ya.M., Exogenous Epigenetic Uranium Deposits in the Kyzylkum Region and Adjacent Districts, *Geol. Rudn. Mestorozhd.*, 1993, vol. 35, no. 3, pp. 222-245.
- Sochneva, E.G., Leucoxene from Productive Strata of a Deposit in the European Part of the USSR, *Izv. Vyssh. Uchebn. Zaved., Geol. Razved.*, 1970, no. 7, pp. 41-47.

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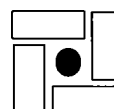
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